U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-261 917

Technology and Economics of Flue Gas NOx Oxidation by Ozone

Research Triangle Inst, Research Triangle Park, N C

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

Dec 76

PB 261 917

EPA

EPA-600/7-78-030
December 1978

TECHNOLOGY AND ECONOMICS OF FLUE GAS NO_x OXIDATION BY OZONE

Interagency
Energy-Environment
Research and Development
Program Report

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into seven series. These seven broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The seven series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development

This report has been assigned to the INTERAGENCY ENERGY-ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA's mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally--compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide range of energy-related environmental issues.

REVIEW NOTICE

This report has been reviewed by the participating Federal Agencies, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Government, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-76-033	2.
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE Technology and Economics of Flue Gas NOx Oxidation by Ozone	5. REPORT DATE December 1976
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) J.W. Harrison	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709	10. PROGRAM ELEMENT NO. EHE624
	11. CONTRACT/GRANT NO. 68-02-1325, Task 38
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED Task Final; 7-10/76
	14. SPONSORING AGENCY CODE EPA-ORD

15. SUPPLEMENTARY NOTES IERL-RTP task officer for this report is R.D. Stern, 919/549-8411 Ext 2915, Mail Drop 61.

16. ABSTRACT The report gives results of an investigation of the kinetics of oxidation of NO by ozone and concludes that a stoichiometric amount of ozone is required when oxidation occurs at flue gas temperatures typical for electrical generating stations. It also surveys the state of current technology for large-scale ozone generation and concludes that electrical discharge is the only feasible method at present. The report also presents results (on a per unit basis) of calculations of the energy consumption and economics of ozone generation at rates sufficient to oxidize NO at flue gas flow rates and at nitrogen oxides (NOx) concentrations typical for 500 MW coal- and oil-fired boilers. Stationary combustion sources contribute about half the man-made NOx emitted to the atmosphere in the U.S. Flue gas from combustion processes contains NOx which is predominantly in the form of NO. Although NO2 is to some extent soluble in water or aqueous solutions, NO is practically insoluble when conventional scrubbing processes are used. For effective removal, the NO must either be reduced to elemental nitrogen or oxidized to NO2 or higher oxides which can be removed by scrubbing.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Flue Gases Nitrogen Oxides Oxidation Ozone Kinetics Electric Power Plants Coal Fuel Oil	Air Pollution Control Stationary Sources	13B 10B 21B 21D 07B 20K

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Unlimited	Unclassified	
	20. SECURITY CLASS (This page) Unclassified	

EPA Form 2220-1 (9-73)

EPA-600/7-76-033
December 1976

TECHNOLOGY AND ECONOMICS OF FLUE GAS NO_x OXIDATION BY OZONE

by

J.W. Harrison

Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709

Contract No. 68-02-1325, Task 38
Program Element No. EHE624

EPA Task Officer: Richard D. Stern

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

TABLE OF CONTENTS

	Page
LIST OF FIGURES	iv
LIST OF TABLES	v
INTRODUCTION	1
EXECUTIVE SUMMARY	3
ESTIMATE OF OZONE REQUIREMENT	6
OZONE GENERATION TECHNOLOGY AND ENERGY REQUIREMENTS	11
Corona Discharge Generation of Ozone	11
Ozone Generation Systems	14
Utility Requirements	18
ECONOMICS OF OZONE PRODUCTION	23
FORECAST FOR IMPROVEMENTS	29
APPENDIX A. OZONE REACTION KINETICS	31
Ozone Thermal Decomposition	31
Reaction with Nitric Oxide	33
Reaction with Nitrogen Dioxide	33
Summary	38
APPENDIX B. DETERMINATION OF OZONE DEMAND	40
Model Reactor	40
Approximate Equations	42
Solution of Approximate Equations	45
Steady State Approximation	51
APPENDIX C. ECONOMIC ANALYSIS	57
Capital Costs	57
Operating Costs	61
REFERENCES	65

LIST OF FIGURES

		Page
Figure 1.	Required ozone mass flow rate for oxidation of NO at various concentration at typically flue gas flow rates	10
Figure 2.	Welsbach ozonator (Type C)	13
Figure 3.	Effect of varying oxygen flow	15
Figure 4.	Ozone production versus cooling water inlet temperature (air and oxygen feed)	16
Figure 5.	Ozone generation systems	17
Figure 6.	Utility requirements, power, water, and supply air for ozonator using air feedstock	20
Figure 7.	Utility requirements, power and water, and oxygen feed rate for ozonator and oxygen plant combined	21
Figure 8.	(Concentration, time) curves for ozone + SO_2 reaction showing H_2SO_4 aerosol formation on the addition of cis-pent-2-ene	37
Figure 9.	Elemental reaction volume in plug-flow reactor model	41
Figure 10.	Relation between NO, NO_2 and N_2O_5 concentrations and the fraction of ozone used for oxidation for initial conditions $[O_3]/[NO] = 0.5$ and $[NO_2]/[NO] = 0.05$	47
Figure 11.	Relation between NO, NO_2 and N_2O_5 concentrations and the fraction of ozone used for oxidation for initial conditions $[O_3]/[NO] = 0.9$ and $[NO_2]/[NO] = 0.05$	48
Figure 12.	Relation between NO, NO_2 and N_2O_5 concentrations and the fraction of ozone used for oxidation for initial conditions $[O_3]/[NO] = 1.0$ and $[NO_2]/[NO] = 0.05$	49
Figure 13.	Relation between NO, NO_2 and N_2O_5 concentrations and the fraction of ozone used for oxidation for initial conditions $[O_3]/[NO] = 1.0$ and $[NO_2]/[NO] = 0.05$	50
Figure 14.	Relation between NO and NO_2 concentrations and the fraction of ozone used for initial conditions $[O_3]/[NO] = 1.0$ and $[NO_2]/[NO] = 0.05$ with steady state assumption for $[N_2O_5]$	54
Figure 15.	Cost of cooling water versus flow rate	62

LIST OF TABLES

		Page
Table 1.	Summary of Capital and Operating Costs and Energy Requirements for Flue Gas NO Oxidation by Ozone for 500 MW Oil-Fired and Coal-Fired Plants	4
Table 2.	Estimated Flue Gas Compositions for Power Units without Emission Control Facilities	7
Table 3.	Power Plant Flue Gas Emission Rates	9
Table 4.	Ozone Generation by Various Methods, Best Reported Results	12
Table 5.	Utility Requirements for Ozone Generation for NO Oxidation in Flue Gas from 500 MW Oil-Fired and Coal-Fired Stations	22
Table 6.	Assumed Power Plant Capacity Schedule	24
Table 7.	Cost Items and Estimated Total Capital Investment for Ozonation Facilities for 500 MW Coal-Fired and Oil-Fired Generation Stations	26
Table 8.	Annual Operating Costs, First Year, 7,000 Operating Hours for Oxidation of NO in Flue Gas of 500 MW Generating Units	27
Table 9.	Size of Reaction Rate Values at 60° and 149°C	43
Table 10.	Numerical Estimates for Initial Values at 149°C of Terms in Rate Equations at Stoichiometric Ozone Feed from Both Air Stock and Oxygen Stock	44
Table 11.	Estimated Direct Capital Costs for Ozone Generation for NO Oxidation in 500 MW Generating Stations	59
Table 12.	Indirect Investment and Allowance Factors	60
Table 13.	Project Expenditure Schedule	60
Table 14.	Direct Cost Elements for Operation of Ozonators and Oxygen Plant	63
Table 15.	Annual Capital Charges for Power Industry Financing	64

INTRODUCTION

Stationary combustion sources contribute about one-half of the man-made nitrogen oxides (NO_x) emitted to the atmosphere in the United States. Because these emissions contribute to adverse health effects, EPA is pursuing a vigorous program of research into cost-effective, commercially viable methods for controlling these emissions. Two branches of control technology are being addressed: (1) control of the combustion process (combustion modification) and (2) control of post-combustion products (flue gas treatment-FGT). Due to recent emphasis on NO_x emission control and because FGT can be employed as an "add-on" technology, particularly when high removal efficiencies are required or when combustion modification is inappropriate, there has been an increased activity of EPA research in this area.

Flue gas from combustion processes contains NO_x which is predominantly in the form NO. Although NO_2 is to some extent soluble in water or aqueous solutions, NO is practically insoluble as far as conventional scrubbing processes are concerned. Therefore, for effective removal NO must be either reduced to elemental nitrogen, or oxidized to NO_2 or N_2O_5. This leads to two types of control options: NO reduction or NO oxidation followed by NO_2 scrubbing.

At normal flue gas exit temperatures (about 300°F or 150°C) the oxidation of NO by atmospheric oxygen is kinetically controlled at too low a rate for practical conversion to NO_2 or N_2O_5. Therefore, some strong oxidant such as ozone or chlorine dioxide must be used to insure a practical reaction velocity. The resulting reaction products have, at present, little or no commercial value to offset expensive, relatively complex equipment required and the projected high operating costs. Despite these drawbacks, however, processes involving NO oxidation followed by NO_2 wet scrubbing are being developed in Japan due to the more stringent regulations on NO_x control and the potential for simultaneous SO_2 and NO_x removal.

This report analyzes one of the NO oxidation process options which involves the conversion of NO to NO_2 or N_2O_5 by gas phase reaction with ozone. The objectives of the analysis are: to determine the amount of ozone required per unit of NO in a typical flue gas stream; to determine the costs and energy requirements of ozone generated using current technology; and to determine whether or not any significant improvements in ozone generation technology can be forecast. This information provides the basis for assessment of whether or not this method of NO oxidation is cost-effective and commercially viable when compared to alternative oxidation methods.

EXECUTIVE SUMMARY

Consideration of the reactions that take place between ozone (O_3) and nitric oxide (NO), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) in a typical flue gas stream from a generation unit indicate that to a good approximation only an amount of ozone stoichiometric with the NO_x is required to achieve essentially complete conversion of NO to either NO_2 or N_2O_5, both of which may be subsequently scrubbed from the gas stream. The reaction with SO_2 is negligible.

The only viable method currently available for large scale ozone generation is the corona discharge. Either air or oxygen can be used as feedstock to the ozone generator. With oxygen feed the output ozone concentration is approximately twice that with air feed and the electrical energy required per kilogram of ozone produced is approximately half that with air feed. However, when the energy required to produce oxygen from air is taken into account, the total energy requirement using oxygen feed is found to be higher than that for air feed.

The energy requirements and the capital and operating costs were examined for ozone generation with air and oxygen as feed for a 500 MW oil-fired and coal-fired unit. The results are summarized in Table 1. Approximately 13% more energy is required for generation from oxygen. Even with air feed the energy penalty for ozone oxidation of NO is sizeable. From 3% to over 9% of the total energy generated by the plant may be required for ozone generation, depending upon the NO concentration.

In addition to a higher energy penalty, both capital investment and operating costs are much higher for ozone generated from oxygen than from air. As can be seen from Table 1, the capital investment for ozone generation from oxygen feed is about three times as large as that required for air feed. For the NO concentrations typical for an oil-fired unit approximately $56 of capital investment is required per kWh of generating capacity for an oxygen feed ozonator compared to about $18 per kWh capacity for an air feed unit. At the much higher NO levels typical of coal-fired generating stations the capital investment jumps to about

Table 1. Summary of Capital and Operating Costs and Energy Requirements for Flue Gas NO Oxidation by Ozone for 500 MW Oil-Fired and Coal-Fired Plants

Item	Oil Fired (200 ppm NO)		Coal Fired (600 ppm NO)	
	Air Feed	Oxygen Feed	Air Feed	Oxygen Feed
Capital Investment				
$/kg O_3/yr	1.85	5.90	1.84	5.34
$/KW capacity	17.60	56.20	52.60	152.40
Operating Rates				
$/kg O_3 produced	1.48	2.76	1.16	2.24
mil/kWh produced	2.0	3.8	4.7	9.1
Energy				
kWh/yr O_3 production	1.1×10^8	1.25×10^8	3.3×10^8	3.75×10^8
% Energy for O_3 production	3.1	3.6	9.4	10.7

$152 per kWh capacity when oxygen feed is used compared to about $53 per kWh for air feed.

There is a similar disparity in operating costs. As can be seen from Table 1, operating costs for oxygen feed ozonators are approximately twice as large as those for air feed units. For oil-fired units the operating rates are 3.8 mil per kWh produced when oxygen feed is used compared to 2 mil per kWh when air feed is used. Again, for the higher NO concentrations typical of coal-fired generators, operating rates for these installations would be much higher, 9.1 mil per kWh for oxygen feed or 4.7 mil per kWh for air feed. The economic and energy penalties associated with large scale ozone generation increase with increasing NO content. The use of combustion modification technology to reduce NO concentration prior to post combustion FGT processes, such as the oxidation process analyzed in this report, would be highly desirable, if not obligatory, if ozone oxidation is to be seriously considered. In this connection, it must be emphasized that the costs and energy requirements have been determined exclusively for the generation of ozone for supply to the flue gas stream. They do not include the cost of building and operating scrubbers for NO_2 removal.

At present the only practical improvement in ozone generation technology appears to be the possibility of reducing the energy required by eliminating the necessity for air preparation (filtering, dehumidifying) prior to induction into the ozonator. A process for this has reportedly been developed in Japan, but is not yet available in this country. The energy required per kilogram of ozone produced is about two-thirds that now required. Elimination of the air clean-up equipment should also provide a savings in capital investment and, possibly, reduced maintenance costs. Until such a system is proved in large scale operation, however, it appears that the use of ozone for NO oxidation will be very expensive.

ESTIMATE OF OZONE REQUIREMENT

A recent report[1] on NO_x abatement for stationary sources in Japan has given some details on the use of ozone to promote NO_x removal in two pilot plant evaluations. Both of these plants use ozone to oxidize NO to NO_2 or N_2O_5 followed by scrubbing to remove the higher oxides from the treated gas stream. Although some economic data are given the model upon which the estimates are based is not given, making it difficult to extrapolate to typical full-sized generation units. In order to make a realistic assessment of the ozone requirements for a typical power plant in the United States, a model situation will be analyzed in this report. The physical situation assumed is that the ozone is generated on-site and injected into the flue gas stream where the gas phase reactions of ozone (O_3) with other chemical species in the gas stream occur in a manner that is typical of "plug-flow" reactors[2]. This model assumes that conversion of reactants at the walls is negligible compared to the gas phase reaction rates and that these gas phase reactions occur as the reactants are transported in the streaming gas.

The flue gas will contain appreciable amounts of N_2, CO_2, and H_2O vapor, smaller amounts of O_2, and even smaller amounts of SO_2, NO and NO_2. (See Table 2). Typically the injected ozone stream will consist of about 1 to 2% of ozone in either air or oxygen, depending on which gas is used as feedstock for the ozone generator. Among these gas phase constituents the major conversion mechanisms for ozone are thermal decomposition, oxidation of NO to NO_2 (the desired reaction), oxidation of NO_2 to N_2O_5, catalyzed decomposition of ozone by N_2O_5 and oxidation of SO_2 to SO_3. These reactions and their relative rates are discussed in Appendix A. Under the conditions assumed, the conversion of NO to NO_2 and the conversion of NO_2 to N_2O_5, followed by reaction of NO with N_2O_5, are the predominant reactions.

The plug-flow model reactor analysis detailed in Appendix B, using the reaction rate data given in Appendix A, indicates that the amount of ozone required for essentially complete removal of NO from the gas stream

Table 2. Estimated Flue Gas Compositions for Power Units without Emission Control Facilities.[3]

Fuel and boiler type	Coal-fired boiler pulverized coal (horizontal, frontal-fired)(1)			Oil-fired boiler (tangential-fired)(2)		
Sulfur content of fuel, % by wt	2.0	3.5	5.0	1.0	2.5	4.0
Flue gas composition, % by volume						
Nitrogen	74.62	74.55	74.49	73.83	73.73	73.64
Carbon dioxide	12.57	12.55	12.54	12.52	12.37	12.21
Oxygen	4.86	4.85	4.85	2.55	2.55	2.54
Water	7.77	7.76	7.75	11.03	11.19	11.37
Sulfur dioxide	0.12	0.22	0.31	0.05	0.14	0.22
Nitrogen oxides	0.06	0.06	0.06	0.02	0.02	0.02
Fly ash loading						
Grains/scf dry	4.11	4.11	4.11	0.036	0.036	0.036
Grains/scf wet	3.79	3.79	3.79	0.032	0.032	0.032

(1) Pulverized coal, 20% excess air to boiler, 13% additional air leakage at heater assumed.

(2) Assumed 5% excess air to boiler and 10% air leakage to preheater.

by conversion to NO_2 is that required by the stoichiometric equation

$$NO + O_3 = NO_2 + O_2 \ . \qquad (1)$$

This conclusion allows an estimate of the amount of ozone that must be used for a given plant size.

An equation is derived in Appendix B for the mass flow rate of ozone required for a given flue gas flow rate and NO concentration. This equation is

$$w_{O_3} = 2 \times 10^{-6} Q_F \eta \quad kg/s \qquad (2)$$

where Q_F is the flue gas flow rate in m^3/s at the standard condition of one atmosphere and 21°C (about 70°F), and η is the NO concentration in ppm. Table 3 shows flue gas flow rates typical of 200 MW, 500 MW and 1000 MW power plants. For purposes of estimating, the respective flow rates will be taken as 188 m^3/s (4×10^5 SCFM), 472 m^3/s (1×10^6 SCFM) and 944 m^3/s (2×10^6 SCFM). Using these nominal rates the ozone requirement as a function of NO concentration is given in Figure 1.

As pointed out in Appendix B, this estimate does not take into account ozone lost due to catalyzed decomposition on the hot surfaces of the duct in which the gas streams are mixed and the reaction takes place. However, it does provide a reasonable basis for assessing the size of ozone generation plant required to produce ozone at the rates necessary for present day electrical generating stations in the United States. The next section examines current ozone generation technology in order to determine the capability of generating ozone in the large amounts required and the price to be paid in terms of energy and dollars for NO oxidation by this method.

Table 3. Power Plant Flue Gas Emission Rates.[3]

Power plant size, MW	Type plant	Stack gas flow acfm (310°F)	scfm (70°F)	m^3/s(21°C)
Coal-fired units				
200	New	630×10^3	620×10^3	203
500	New	$1,540 \times 10^3$	$1,060 \times 10^3$	500
1,000	New	$2,980 \times 10^3$	$2,060 \times 10^3$	972
Oil-fired units				
200	New	530×10^3	364×10^3	172
500	New	$1,300 \times 10^3$	908×10^3	428
1,000	New	$2,510 \times 10^3$	$1,720 \times 10^3$	812

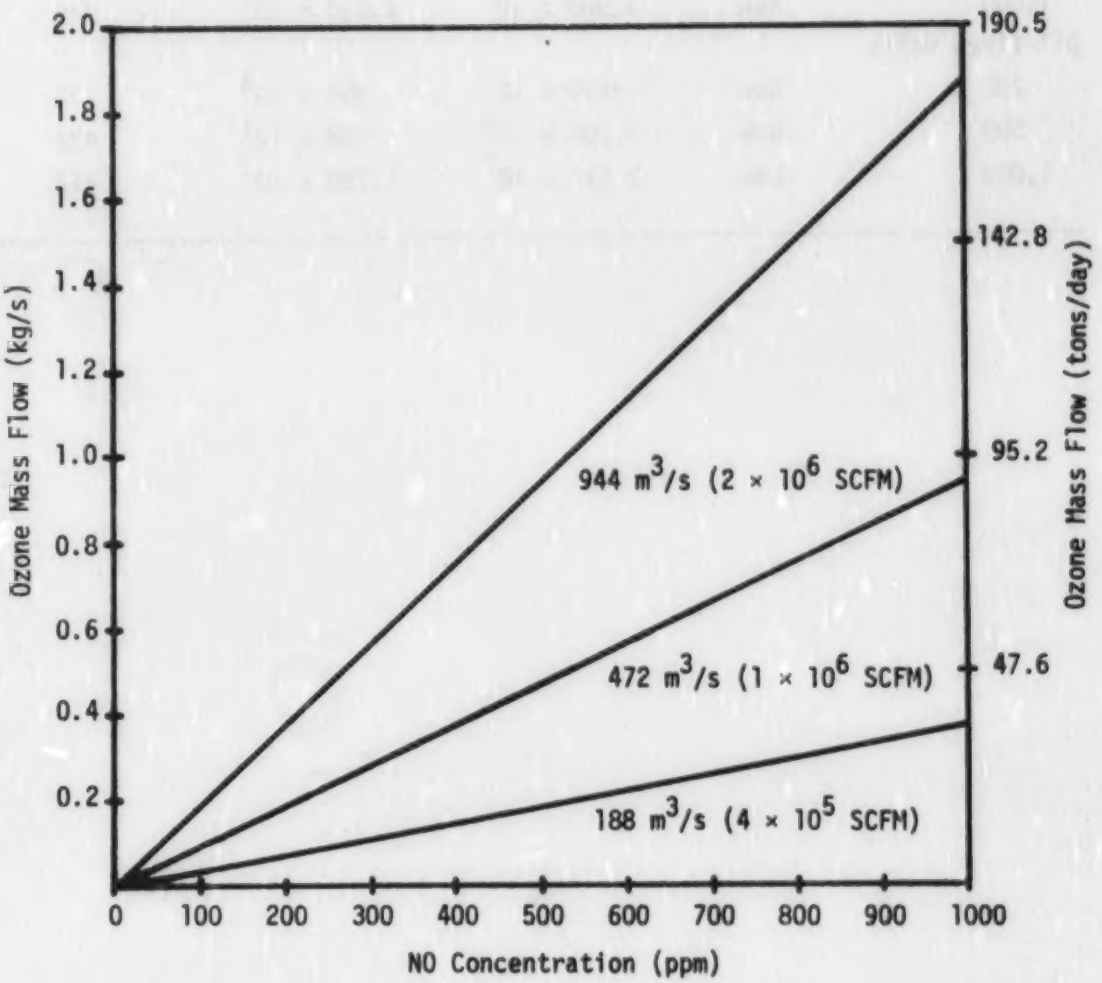

Figure 1. Required ozone mass flow rate for oxidation of NO at various concentrations for typical flue gas flow rates.

OZONE GENERATION TECHNOLOGY AND ENERGY REQUIREMENTS

Generation of ozone from a gas containing oxygen requires a rupture of the O_2 bond. At 25°C the bond dissociation energy is about 5.2 electron volts (8.3×10^{-19} Joule per molecule or about 5×10^5 Joules/mole).[4] Several methods of producing this dissociation, followed by the generation step

$$O + 2\,O_2 \rightarrow O_3 + O_2 \qquad (3)$$

are summarized in Table 4 along with the yield in kilograms of ozone per kilowatt-hour of energy input.[5] Also shown is the ozone concentration available in the output stream. It should be noted that the maximum yields are obtained by operating at much less than the maximum output ozone concentrations. This will be discussed further in the next section. Of all of these methods, the only one currently viable for large scale generation of ozone is the corona discharge.

Corona Discharge Generation of Ozone

The status of large scale ozone generation technology ca. 1973 has been surveyed by Klein *et al.*[6] According to Klein the large scale units all use a corona discharge method. For this method the major design parameters are air gap, pressure, temperature, dielectric covering the electrodes, electric power voltage and frequency, feed gas composition and output ozone concentration. Typically the latter varies from less than 0.5% to as high as 10% by weight for a well designed generator operating under ideal conditions. There is an inverse relationship between power efficiency (kgO_3/kWh) and ozone concentration.

A typical large scale ozonator[5] is shown schematically in Figure 2. The outer tubes, end plates and pressure vessel are stainless steel. The inner tubes are glass, coated internally with either graphite or metal for the second electrode. The applied potential is 15,000-19,000 volts at 60 Hz. The power density is 650-1300 Watts per square meter of electrode area. Either air or oxygen is used as a feed, supplied with

Table 4. Ozone Generation by Various Methods, Best Reported Results.[5]

	Yield, kgO_3/kWh	Ozone Concentration* (% Volume)
theoretical	0.346	
corona discharge in air or oxygen	up to .150	up to 6%
electrolysis of water	up to .012	up to 20%
photochemical		
-2537 Å	up to .025	up to 0.25%
1400-1700 Å		up to 3.5%
radiochemical		
using O_2 gas	.220	.006%
using liquid O_2	.108	5%
thermal	.056	0.33%

*Maximum yields can, of course, only be obtained by operating at much less than the maximum ozone concentrations.

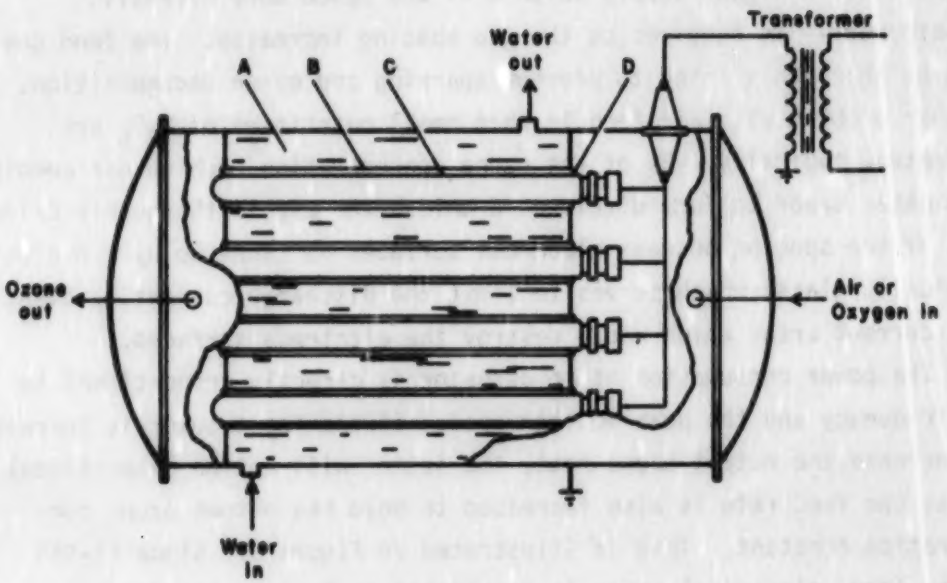

Figure 2 . Welsbach ozonator (Type C). Legend: A, cooling water; B, stainless-steel tube; C, discharge gap; D, glass tube.[5]

with a dewpoint of at least -60°C. Internal pressure is maintained at 1-2 atmospheres to optimize the conversion efficiency. With air feed, the output ozone concentration is typically about 1% by weight at a yield of 0.05-0.06 kgO_3/kWh. With oxygen feed the output ozone concentration is typically 1.5-2.0% by weight at a yield of 0.11-0.13 kgO_3/kWh. These yield figures are only for the ozonators. They do not include energy for pumping and drying air (for air feed) or liquefaction (for oxygen feed).

Electrode gap spacing must be large enough not to cause too high a pressure drop as feed gas is pumped through the reactor, but not too large, since a higher supply voltage -- and hence more expensive transformer -- is required as the gap spacing increases. The feed gas must be thoroughly dried to prevent sparking and ozone decomposition. Another problem with air feed is that small quantities of N_2O_5 are generated, typically 1-2% of the ozone concentration[5], which can combine with water vapor to form nitric acid unless the air is thoroughly dried. Part of the spacing between electrode surfaces is taken up by a dielectric (typically glass) which serves to limit the discharge current, preventing high current areas which would destroy the electrode surfaces.

The power consumption of an ozonator is directly proportional to the frequency and the peak voltage used. If the input power is increased to increase the output ozone rate, the latter will not be proportional unless the feed rate is also increased to hold the output ozone concentration constant. This is illustrated in Figure 3. Since 85-95% of the input electrical power is dissipated as heat in the discharge space, increased power requires concomitant increase in coolant flow to avoid excessive temperature rise, which as discussed in Appendix A, can lead to more rapid ozone decomposition. The effect of increasing inlet temperature of cooling water on ozone production at a given oxygen or air feed rate is shown in Figure 4. It can be seen that an adequate supply of cooling water is necessary for efficient operation.

Ozone Generation Systems

Basic process flow diagrams for two types of ozone generation systems are shown in Figure 5. When air is used as the feedstock it

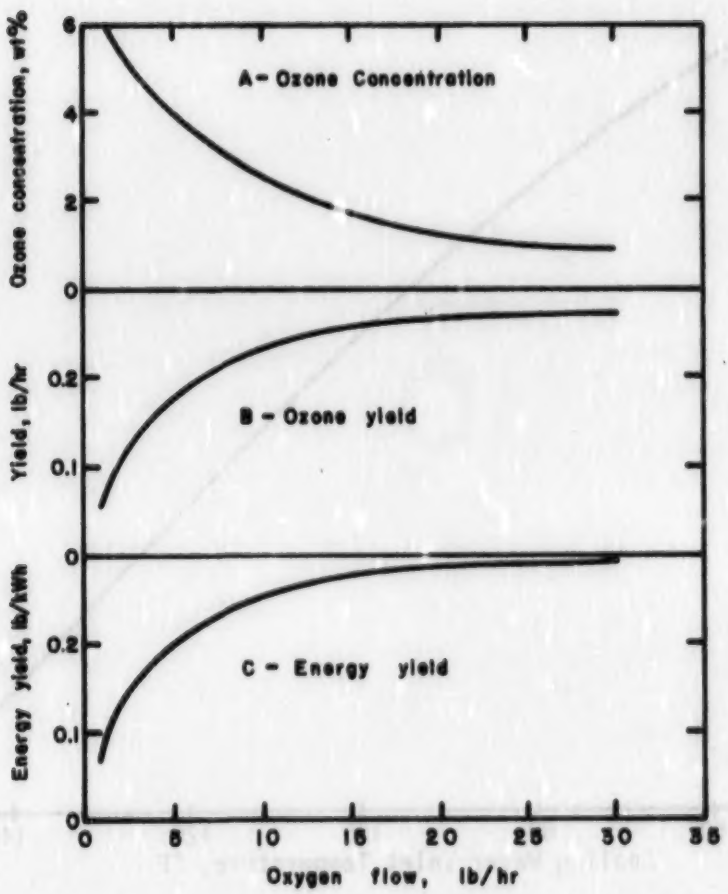

Figure 3. Effect of varying oxygen flow.[5]

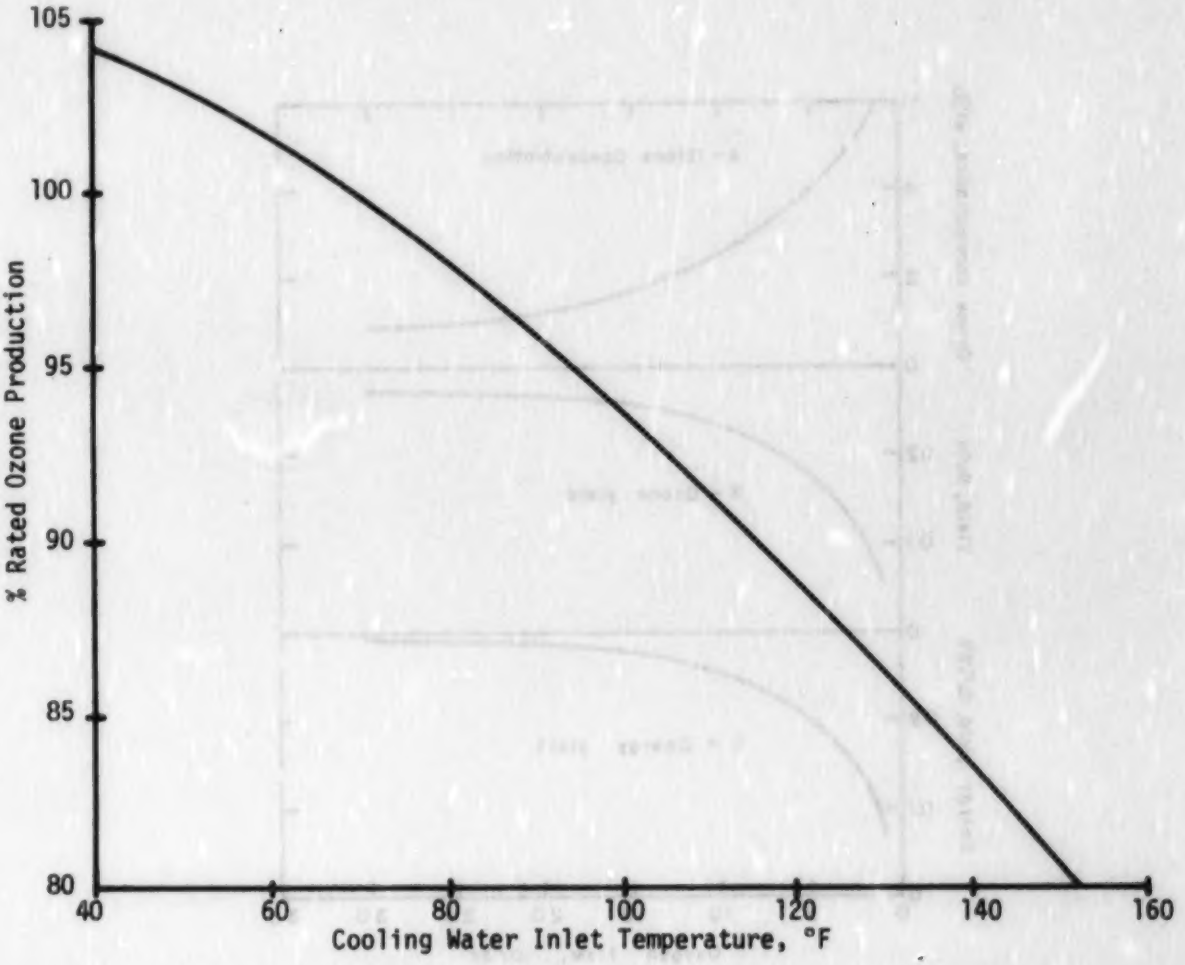

Figure 4. Typical effect on ozone production of cooling water inlet temperature (air and oxygen feed).[7]

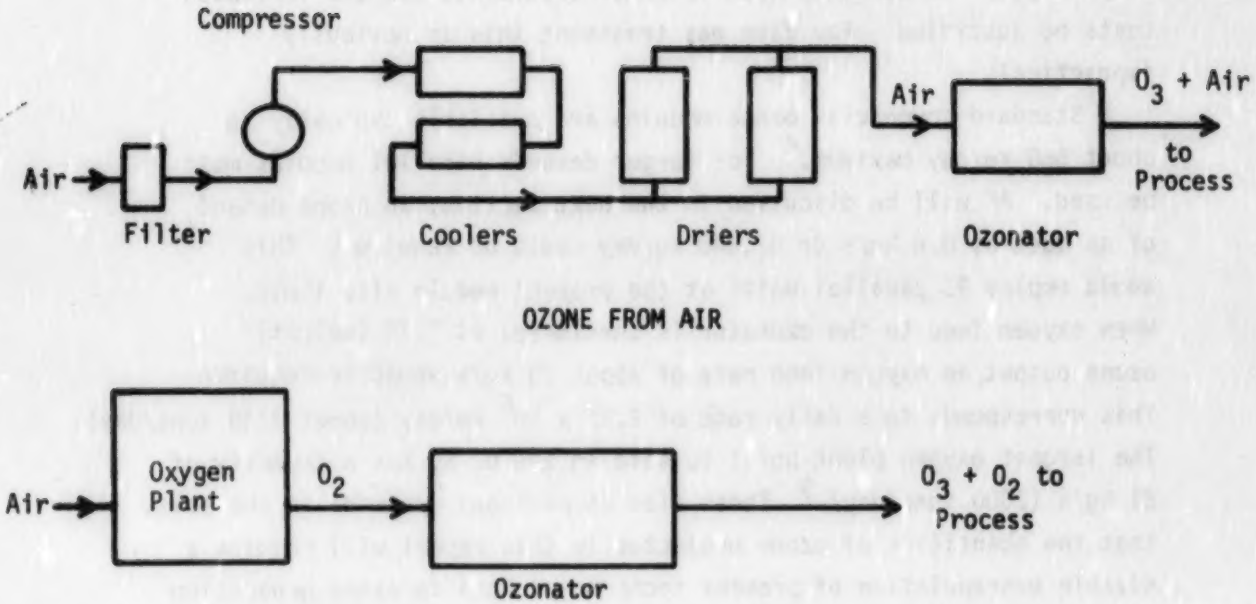

Figure 5. Ozone generation systems.[7]

must be filtered to remove particulate matter, cooled to minimize thermal decomposition of ozone in the ozone generator (ozonator) and dried to remove practically all of the moisture prior to insertion into the corona discharge unit.

For large scale generation from oxygen feedstock, a plant producing oxygen from air must be used. This has the advantage of producing a higher percentage of ozone in the output stream of the ozonator for a given flow rate, but this advantage is offset by the increased complexity, capital and operating costs of the oxygen plant. Only if the oxygen is used in some other manner, for instance by recycling, as is commonly used in water treatment, can the increased costs be justified. For flue gas treatment this is obviously impractical.

Standard commercial ozone modules are available typically to about 560 kg/day maximum.[8] For larger demands parallel modules must be used. As will be discussed in the next section, an ozone demand of as much as 0.6 kg/s or 51,840 kg/day could be required. This would employ 93 parallel units at the present module size limit. When oxygen feed to the ozonator is considered at 1.7% (weight) ozone output, an oxygen feed rate of about 33 kg/s would be required. This corresponds to a daily rate of 2.85×10^6 kg/day (about 3140 tons/day). The largest oxygen plant built to date in the U. S. has a capacity of 21 kg/s (2000 tons/day).[9] These size comparisons are made to emphasize that the quantities of ozone projected in this report will require a sizable extrapolation of present technology, both in ozone generation and in oxygen liquefaction (should this be used). This extrapolation should be kept in mind when the economics of ozone production are discussed in a subsequent section.

Utility Requirements

Using the ozone mass flow requirement data from Figure 1 along with typical yield figures for ozone generators and typical cooling water flow rates, an estimate can be obtained for the electrical energy, water and air (or oxygen) demands which these ozone flow rates imply.

The electrical power required, both for ozone generation and for air induction and conditioning, is typically 23.15 kWh/kgO_3 for 1% (weight) ozone output when air is used as a feedstock to the ozonator.[8] Required power as a function of ozone mass flow rate is plotted in Figure 6. Also shown in this figure are the cooling water flow rate required, based on an estimate of .0162 ℓ/s per kgO_3 produced[7], and the flow rate of air required, based on the weight fraction.

For oxygen feed to the ozonator, approximately the same cooling water flow would be required but the power requirement would be reduced to about 8.3 kWh/kgO_3 for 1.7% (weight) ozone output.[7] The power and cooling water requirements for the oxygen plant must be added to these figures. For a typical plant producing 98% oxygen by volume, the power and water requirements are about 0.31 kWh/kgO_2 and 0.039 m^3/kgO_2, respectively. Since the flow rate of oxygen will be about 50 times that of the ozone output, these requirements will be substantial. The combined power and cooling water demand and oxygen demand are plotted versus ozone mass flow rate in Figure 7. Comparison with Figure 6 shows that the higher ozone generating efficiency when using oxygen is more than offset by the power required to extract oxygen from air to obtain the feedstock to the ozonator. Utility requirements for ozone generation are summarized in Table 5.

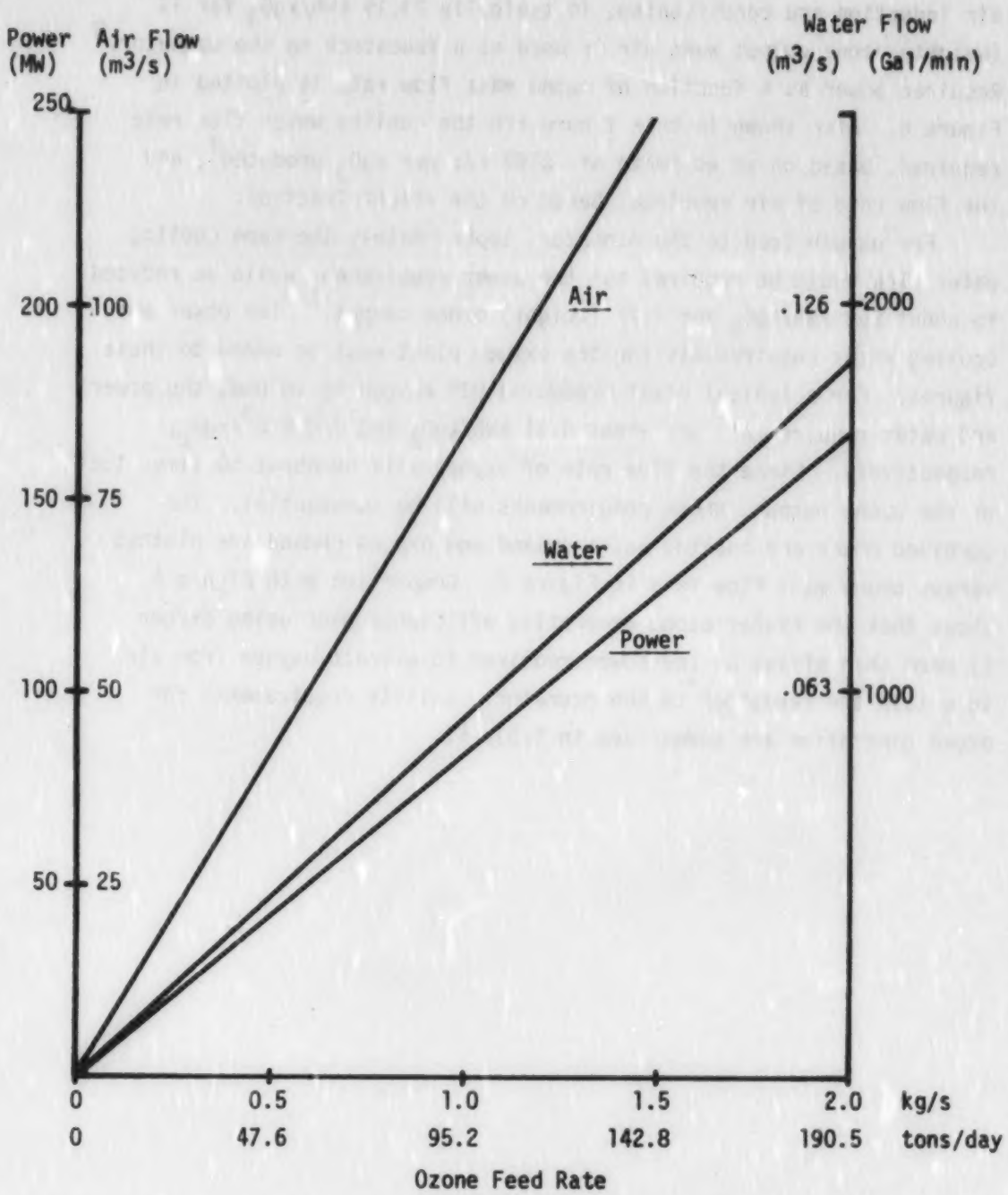

Figure 6. Utility requirements, power, water, and supply air for ozonator using air feedstock.

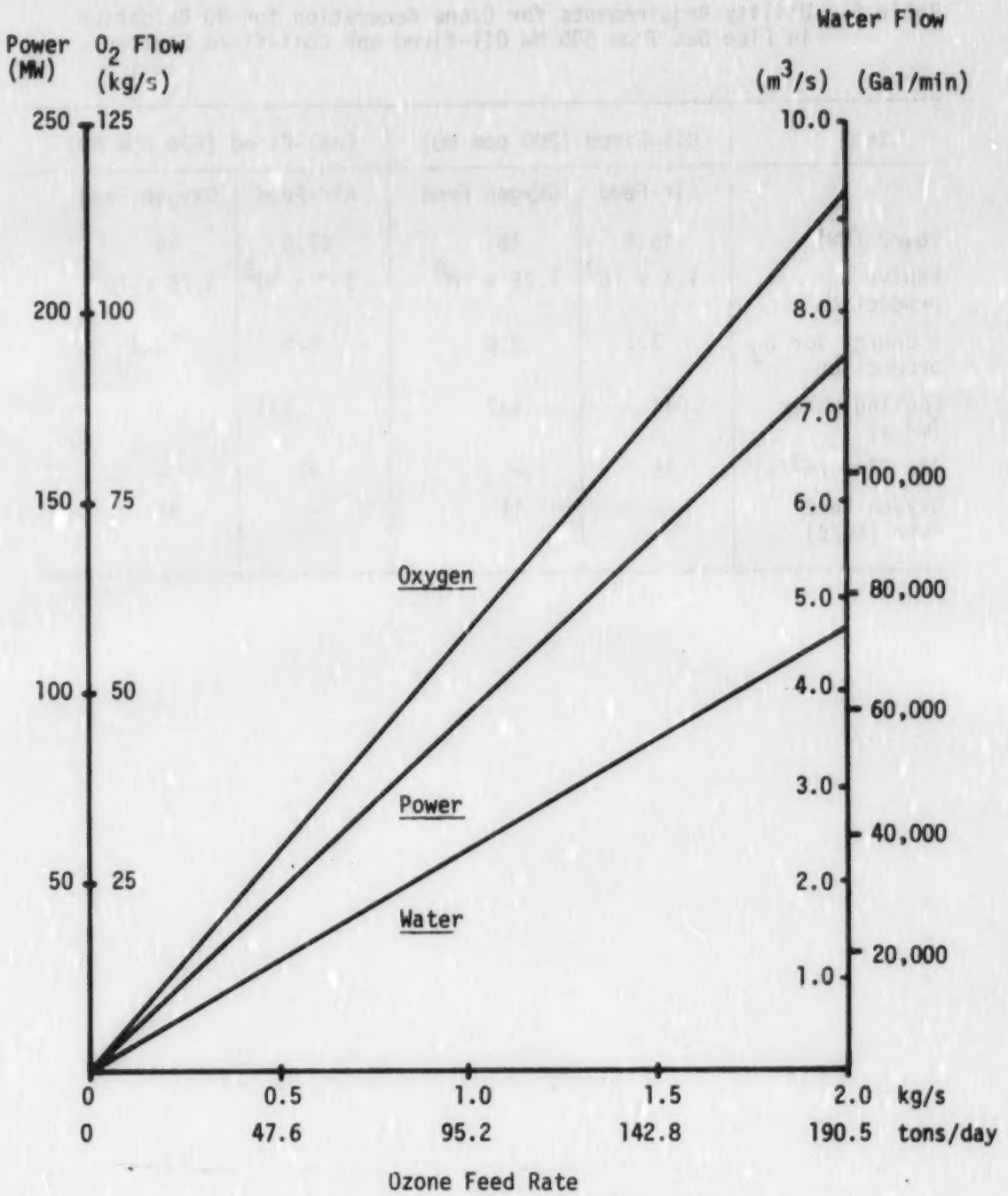

Figure 7. Utility requirements, power and water, and oxygen feed rate for ozonator and oxygen plant combined.

Table 5. Utility Requirements for Ozone Generation for NO Oxidation in Flue Gas from 500 MW Oil-fired and Coal-fired Stations.

Item	Oil-Fired (200 ppm NO)		Coal-Fired (600 ppm NO)	
	Air-Feed	Oxygen Feed	Air-Feed	Oxygen Feed
Power (MW)	15.8	18	47.5	54
kWh/yr O_3 production	1.1×10^8	1.25×10^8	3.3×10^8	3.75×10^8
% Energy for O_3 production	3.1	3.6	9.5	10.8
Cooling water (m^3/s)	.011	.437	.033	1.31
Air Flow (m^3/s)	15.7	-	47	-
Oxygen Feed Rate (kg/s)	-	11	-	33

ECONOMICS OF OZONE PRODUCTION

The economics of integrated ozone water treatment systems has been treated by Rosen,[10] who has discussed the tradeoffs between air feed and oxygen feed systems. However his analysis must be considerably modified for application to power plant FGT systems because oxygen recycle is not possible. Since the ozone FGT systems would be installed primarily in private utility owned electrical generation plants, the guidelines appropriate to regulated private utility-type costing[11] should be employed. These guidelines have been applied to economic evaluations of the costs of power plant flue gas desulfurization processes by McGlamery et al.[3] Their procedure is applicable to the economic evaluation of ozone FGT processes and will be used.

Based on Federal Power Commission guidelines[11] a new fossil-fueled power generation unit has an expected operating life of 30 years. The utilization factor over this period declines rapidly after the first 10 years, as shown in Table 6, which is based on TVA operating data.[3] Recently there has been some discussion of reducing the depreciation lifetime to 20 years in order to internally generate more capital,[15] but whether or not this might occur in the near future is doubtful. Although an analysis could be performed to project operating costs over a 20 year lifetime as well as a 30 year lifetime, at the present exploratory stage of considering the economic viability of the use of ozone to oxidize NO to NO_2 neither course seems justified. Rather, it appears that an assessment of first year costs is all that is needed at present.

In order to provide such an assessment, two model situations are used. The first case is an oil-fired 500 MW unit which is assumed to have an NO concentration of 200 ppm (cf. Table 2). The second is a coal-fired 500 MW unit which is assumed to have an NO concentration of 600 ppm (cf. Table 2). A cost estimate analysis is performed for each case for both air feed and oxygen feed to the ozone generator. Details of this procedure are given in Appendix C.

Capital cost estimates for ozone generators were obtained from a manufacturer.[8] Capital costs for the required oxygen plants were based

Table 6. Assumed Power Plant Capacity Schedule.[3]

Operating year	Capacity factor % (nameplate rating)*	Annual kWh/kW capacity
1-10	80	7,000
11-15	57	5,000
16-20	40	3,500
21-30	17	1,500
Average for 30 year life	48.5	4,250

*100% = 8,760 hours/yr

on manufacturer's data (1974) updated to 1976 dollars using Chemical Engineering magazine cost indices.[12] Size was updated using the standard cost-capacity relation

$$C_2 = C_1(Q_2/Q_1)^N \qquad (4)$$

where C_2 is the cost of a plant with capacity Q_2, and C_1 is the cost of a plant with capacity Q_1. The exponent N has the capacity of 0.72 for oxygen plants in the range .01 to 15.8 kg/s (1 to 1500 tons/day).[13] Because the size of plant required for the coal-fired case was approximately double the upper limit of this range, this limit was used in equation (4) and then the cost was doubled.

Indirect costs covering engineering design and supervision, contractor fees, contingencies and construction field expense were added, as was an allowance for start-up and modification and interest on funds borrowed during the construction phase (assumed to last three years). The resulting total capital costs are given in Table 7

Operating costs, based on 7000 hours of operation in the first year were calculated for direct, indirect and fixed elements. The direct costs were estimated from the utility data presented in the preceding section and from manufacturer's information and/or estimates of operating labor and maintenance costs. Indirect costs were based on the assumption of a plant overhead rate of 20% of the direct costs and an administrative overhead of 10% of the labor cost. Fixed costs were comprised of depreciation (over a 30 year period), replacement, insurance, debt service (10%) equity return (14%) and taxes. Application of these elements give the first year operating costs shown in Table 8.

In both the oil-fired (200 ppm NO) and coal-fired (600 ppm NO) cases the capital and operating costs of using oxygen feed are considerably higher than when air feed to the ozone generator is used. A comparison of the costs for the oil-fired case with those for the coal-fired case show a direct relationship with NO content. This dramatically emphasizes the desirability of using combustion modification controls to reduce NO content prior to flue gas treatment. However, even if combustion

Table 7. Cost Items and Estimated Total Capital Investment for Ozonation Facilities for 500 MW Coal-Fired and Oil-Fired Generating Stations

Item	Oil Fired (200 ppm NO)		Coal Fired (600 ppm NO)	
	Air Feed	Oxygen Feed	Air Feed	Oxygen Feed
Direct Costs	$5.4M	$17.3M	$16.2M	$47.0M
Indirect Costs:				
Engr. Design and Supv.	.49M	1.56M	1.46M	4.23M
Construction Field Expense	.59M	1.90M	1.78M	5.17M
Contractor's Fee	.27M	.87M	.81M	2.35M
Contingency	.54M	1.74M	1.62M	4.70M
Total Direct and Indirect Costs	$7.3M	$23.4M	$21.9M	$63.5M
Allowance for Start-up and Modification (8%)	.58M	1.87M	1.75M	5.1M
Interest During Construction (12%)	.88M	2.81M	2.63M	7.6M
Estimated Total Capital Investment (1976 $)	$8.8M	$28.1M	$26.3M	$76.2M
Unit Costs				
$/kg$O_3$ (first year)	1.85	5.90	1.84	5.34
$/KW capacity	17.60	56.20	52.60	152.40

Table 8. Annual Operating Costs, First Year, 7,000 Operating Hours, for Oxidation of NO in Flue Gas of 500 MW Generating Units

Item	Oil Fired (200 ppm NO)		Coal Fired (600 ppm NO)	
	Air Feed	Oxygen Feed	Air Feed	Oxygen Feed
Direct Costs				
Electrical	$3.305M	$3.806M	$6.624M	$7.616M
Water	0.158M	0.221M	0.159M	0.663M
Labor	0.149M	0.298M	0.298M	0.447M
Maintenance	0.324M	0.519M	0.972M	1.410M
Total Direct Cost	$3.936M	$4.844M	$8.053M	$10.136M
Indirect Cost	0.802M	0.999M	1.641M	2.072M
Fixed Cost	2.291M	7.314M	6.846M	19.835M
Total	$7.029M	$13.157M	$16.540M	$32.043M
Unit Costs				
$/kg O_3 produced	1.48	2.76	1.16	2.24
mil/kWh produced	2.0	3.8	4.7	9.1

modification could reduce the NO content of flue gas from a coal-fired unit to the level now typical of an oil-fired unit, the capital and operating costs would still be significant.

FORECAST FOR IMPROVEMENTS

Until recently the energy required for large scale generation of ozone at about 1% weight concentration with air feed ranged from about 17 to about 20 kWh/kgO_3.[5] It has been reported[14] that an improved version of the corona discharge system has been developed in Japan, based on a concept produced by the Grace Company. This involves redesign of the ozone generator to handle unprocessed air, thereby eliminating the equipment required for air preparation. The energy required is reported to be 11-13 kWh/kgO_3. Negotiations are currently being conducted by Union Carbide to secure licensing rights to produce ozonators using this process for the U. S. Market.

Recently there have been developments in the combined use of nuclear radiation and electric discharge in order to increase the attainable output concentration of ozone and to improve the energy efficiency. A Japanese patent[15] has described the use of gamma radiation from a Cobalt-60 source to increase the O_3 concentration from 3.5%, for electric discharge alone, to 7% in an oxygen feed stream. The energy per unit mass of ozone produced was decreased from 5.6 kWh/kgO_3 for the electric discharge alone to 3.5 kWh/kgO_3 for the combined nuclear radiation-electric discharge process. It should be pointed out, however, that this was bench scale demonstration.

The use of nuclear radiation for ozone production has been studied in this country for a number of years. Steinberg[16] has summarized much of this research and has examined the economics of "chemonuclear" ozone compared to standard electric discharge plants, using as the basis a 400 ton/day plant. The cost analysis assumed that the nuclear radiation is available from "waste radiation" from an existing nuclear reactor. The use for the ozone generated was assumed to be for waste water treatment. In order to put into perspective the size of radioactive source required when a nuclear reactor is not available, Steinberg estimates that in order to generate 907 kgO_3/day a 19.3 Megacurie Cobalt-60 source would be required. A source of this size would present extremely impractical shielding problems. The chemo-nuclear approach does not use electric discharge to augment the production of ozone.

In summary, it appears that in the foreseeable future the only practical improvement that can be expected in large scale ozone generation technology is a reduction in the generating power to about two-thirds of the amount now required, based on the W. R. Grace development.

APPENDIX A. OZONE REACTION KINETICS

The use of ozone to oxidize flue gas NO_x to more readily absorbed species requires the generation of large quantities of ozone. In order to model the process to ascertain the energy efficiency and cost and to forecast the possibility of technological improvements, the reactions and kinetic factors involved in the generation, transport, mixing, and reaction of ozone must be considered.

Ozone Thermal Decomposition

Even as ozone is being generated and transported to the region where it will be used, ozone is in the process of decomposing due to collisions with other gas phase species. The sequence of reactions leading to this decomposition is believed to be[17]

$$O_3 + M \xrightarrow{K_1} O_2 + O + M \qquad (A.1)$$

$$O_2 + O + M \xrightarrow{K_2} O_3 + M \qquad (A.2)$$

$$O + O_3 \xrightarrow{K_3} 2\,O_2 . \qquad (A.3)$$

In these equations M represents a third collision partner, of any type molecule present in the gas mixture. The concentration of M is equal to the number density of gas molecules and is therefore proportional to the total pressure of the gas mixture containing the ozone and oxygen. These are uncatalyzed gas phase reactions. The rate equation for the decay of ozone concentration is

$$\frac{-d[O_3]}{dt} = \frac{2K_1K_3[O_3]^2[M]}{K_2[O_2][M] + K_3[O_3]} . \qquad (A.4)$$

In a practical ozone system the concentration of oxygen is large compared to that of ozone, and the total pressure is usually one to two atmospheres.[5] Comparing the two terms in the denominator at 300°K under typical operating conditions

$$K_2[O_2][M] \approx 2.2 \times 10^5 \text{ sec}^{-1}$$

$$K_3[O_3] \approx 6.1 \times 10^2 \text{ sec}^{-1} .$$

Therefore, to a good approximation

$$\frac{-d[O_3]}{dt} = 2K_1K_3[O_3]^2/K_2[O_2] . \qquad (A.5)$$

or

$$-\frac{d[O_3]}{dt} = K_5[O_3]^2/[O_2] ,$$

where[21] $K_5 = 4.55 \times 10^{15} \exp(-15{,}400/T) \text{ sec}^{-1}$. Note that since [M] no longer appears in the equation, the ozone decomposition rate is not explicitly a function of the total pressure and depends only upon the ozone and oxygen concentrations.

The inverse dependence of decay rate on oxygen concentration suggests the use of oxygen rather than air as the source gas in the ozone generating system. Another reason for not using air is the possibility of catalyzed decomposition of ozone by N_2O_5 through a cyclic process which regenerates N_2O_5 while destroying ozone,[5] which is considered subsequently in this Appendix.

Many solid surfaces catalyze the decomposition of ozone. Catalytic activity depends upon the physical and chemical state of the solid surface as well as upon the presence of moisture.[5] Ozone decomposition in aqueous solutions is much more rapid than in the gaseous state because it is catalyzed by hydroxyl ions.[5]

Reaction with Nitric Oxide

Ozone reacts with nitric oxide to give either electronically excited NO_2^* or vibrationally excited NO_2^+ as

$$NO + O_3 \xrightarrow{K_6} NO_2^* + O_2 \qquad (A.6)$$

$$NO + O_3 \xrightarrow{K_7} NO_2^+ + O_2 \qquad (A.7)$$

with rate constants[18] of $K_6 = 7.8 \times 10^5 \exp(-2103/T)$ m^3/mole-sec and $K_7 = 4.3 \times 10^5 \exp(-1173/T)$ m^3/mole-sec. The electronically excited NO_2 relaxes to ground state either through chemiluminescence or collisional energy transfer, while NO_2^+ relaxes only by the latter mechanism. The combined rate equation for NO_2 is

$$\frac{d[NO_2]}{dt} = K_8 [NO][O_3], \qquad (A.8)$$

where $K_8 = (K_6 + K_7)$. This is also the loss rate for ozone due to NO_2 formation.

Reaction with Nitrogen Dioxide

Ozone reactions with nitrogen dioxide yield N_2O_5 through the reaction sequence[19]

$$NO_2 + O_3 \xrightarrow{K_9} NO_3 + O_2 \qquad (A.9)$$

$$NO_2 + NO_3 \xrightarrow{K_{10}} N_2O_5, \qquad (A.10)$$

the first of which is rate limiting. The rate constant of (A.9) is given by $K_9 = 5.9 \times 10^6 \exp(-3523/T)$ m^3/mole-sec. The N_2O_5 molecules so formed

can thermally decompose and participate in cyclic reaction sequence which decomposes ozone. The complex sequence has been studied in detail[20,21] and elucidated by Johnson.[22] It involves

$$N_2O_5 + M \xrightarrow{a_i(M)} N_2O_5^{i*} + M \qquad (A.11)$$

$$N_2O_5^{i} + M \xrightarrow{b_i(M)} N_2O_5 + M \qquad (A.12)$$

$$N_2O_5^{i*} \xrightarrow{c_i} NO_2 + NO_3 \qquad (A.13)$$

$$NO_2 + NO_3 \xrightarrow{d_i} N_2O_5^{i*} \qquad (A.14)$$

$$NO_2 + NO_3 \xrightarrow{K_{15}} NO + O_2 + NO_2 \qquad (A.15)$$

$$NO + NO_3 \xrightarrow{K_{16}} 2\ NO_2 \qquad (A.16)$$

$$NO_3 + NO_3 \xrightarrow{K_{17}} 2\ NO_2 + O_2 \qquad (A.17)$$

$$NO_2 + O_3 \xrightarrow{K_9} NO_3 + O_2 \qquad (A.9)$$

The superscript i* indicates one of the excited states of N_2O_5. Reaction rates for the individual reactions are appropriately summed over the excited states in order to obtain the overall reaction rate. The rate constants $a_i(M)$ and $b_i(M)$ depend upon the collision partner species M.

Johnston has considered four overall reaction sequences involving (A.9 - A.17). These are, with stoichiometric equations

1. the decomposition of nitrogen pentoxide,

$$2\ N_2O_5 = 4\ NO_2 + O_2 \qquad (A.18)$$

2. the decomposition of nitrogen pentoxide in the presence of nitric oxide,

$$NO + N_2O_5 = 3\ NO_2 \qquad (A.19)$$

3. the decomposition of ozone in the presence of nitrogen pentoxide,

$$2\ O_3 + N_2O_5 = 3\ O_2 + N_2O_5 \qquad (A.20)$$

4. the formation of nitrogen pentoxide from ozone and nitrogen dioxide

$$2\ NO_2 + O_3 = N_2O_5 + O_2\ . \qquad (A.21)$$

All of these mechanisms should be considered in the process under investigation. The second reaction above must be considered when

$$K_{16}[NO] >> K_{15}[NO_2]$$

or (A.22)

$$[NO] >> \frac{K_{15}}{K_{16}}\,[NO_2]\ .$$

Johnston has estimated that, at 300°K, $K_{15} = 7 \times 10^8$ and $K_{16} > 10^{13}$. Therefore, it appears that even trace quantities of NO serve to catalyze the decomposition of N_2O_5. The decay rate is, at the pressure of practical interest,

$$- \frac{d}{dt} [N_2O_5] = K_\infty^{(2)} [N_2O_5] . \qquad (A.23)$$

The value of $K_\infty^{(2)}$ at 300°K is given by Johnston[20] at 0.29 sec^{-1} with an activation energy of $(8.8 \pm 0.84) \times 10^4$ Joule/mole.

The reaction sequence of ozone decomposition by nitrogen pentoxide is given by Johnston[20] as

$$- \frac{d}{dt} [O_3] = K^{(3)} [N_2O_5]^{2/3} [O_3]^{2/3} \qquad (A.24)$$

where $K^{(3)}$ has the value of 2.6 $(mole/m^3)^{1/3}$ sec^{-1} at 300°K with an activation energy of $(8.6 \pm 0.42) \times 10^4$ Joule/mole.

Reaction with Sulfur Dioxide

The reaction of SO_2 with O_3 is very slow unless catalyzed by other species. The reaction

$$SO_2 + O_3 \rightarrow SO_3 + O_2 \qquad (A.25)$$

$$- \frac{d[O_3]}{dt} = K_{21}[SO_2][O_3] \qquad (A.26)$$

has been found[23] to have a rate constant of about 6×10^{-3} m^3/mole-sec at 360°K and about 1.2×10^{-4} m^3/mole-sec at 300°K. In a study of the mecnanism of aerosol formation,[24] it was found that the reaction of SO_2 and O_3 at about 0.1 ppm concentrations in air were very slow until olefins were added to the gas mixture. Then the reaction rates were dramatically increased, leading to the formation of H_2SO_4 aerosol as SO_3 combined with water vapor. This is illustrated in Figure 8. Since it is doubtful that

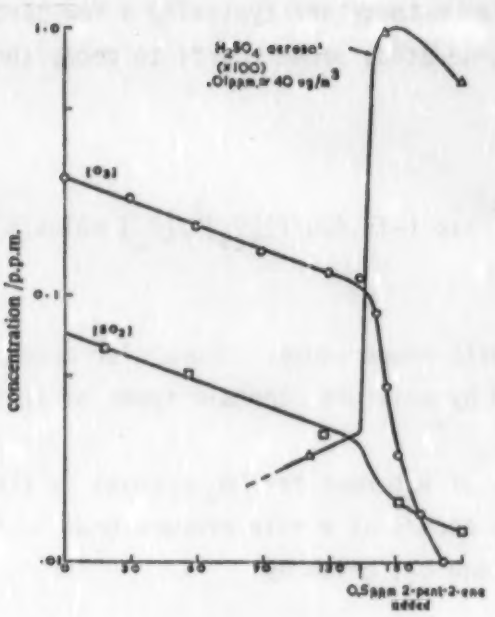

Figure 8. (Concentration, time) curves for ozone + SO_2 reaction showing H_2SO_4 aerosol formation on the addition of cis-pent-2-ene.

any such species would be present in the flue gas, it appears that the oxidation of SO_2 by O_3 represents a negligible depletion of the ozone. Therefore, reaction rate (A.26) will not be included with the other kinetic terms.

Summary

Ozone generation by electrical discharge has poor energy efficiency. Large-scale ozone generator outputs are typically a few percent by weight of ozone at most. Once generated, ozone starts to decay spontaneously at a rate given by

$$-\frac{d[O_3]}{dt} = 4.55 \times 10^{15} \exp(-15{,}400/T)[O_3]^2/[O_2] \text{ moles/m}^3\text{-sec} \qquad (A.27)$$

which rapidly increases with temperature. Ozone also decomposes in reactions which are catalyzed by moisture, certain types of surfaces, and by certain gaseous species.

The primary reaction of interest for NO_x removal is the oxidation of NO to NO_2 by ozone, which occurs at a rate proportional to the gas phase concentration of both NO and O_3, given by

$$\frac{d[NO_2]}{dt} = [7.8 \times 10^5 \exp(-2103/T) + 4.3 \times 10^5 \exp(-1173/T)] \times [NO][O_3] \text{ moles/m}^3\text{-sec}. \qquad (A.28)$$

Ozone also reacts with NO_2 to produce N_2O_5 at a rate proportional to both the NO_2 and O_3 concentrations, given by

$$\frac{d[N_2O_5]}{dt} = 5.9 \times 10^6 \exp(-3523/T)[NO_2][O_3] \text{ moles/m}^3\text{-sec}. \qquad (A.29)$$

The product N_2O_5 is in turn decomposed at a rate which is enhanced by even trace quantities of NO, given by

$$-\frac{d[N_2O_5]}{dt} = 5.77 \times 10^{14} \exp(-10{,}568/T)[N_2O_5] \text{ moles/m}^3\text{-sec}. \quad (A.30)$$

In addition, N_2O_5 participates in a cyclic reaction sequence described by equations (A.11) through (A.17) which tends to decompose ozone at a rate given by

$$-\frac{d[O_3]}{dt} = 2.23 \times 10^{13} \exp(-10{,}316/T)[N_2O_5]^{2/3}[O_3]^{2/3} \text{ mole/m}^3\text{-sec}. \quad (A.31)$$

Compared to reactions with NO_x, the gas phase reaction of ozone with SO_2 is relatively slow. Even though SO_2 typically occurs at concentrations of as much as five to ten times that of NO_x in flue gas from oil- and coal-fired boilers, the rate of loss of ozone due to SO_2 oxidation is negligible compared to other losses.

The rate equations (A.27) through (A.31) are used in Appendix B, evaluated at temperatures typical of flue gas streams, in order to estimate the amount of ozone required to oxidize NO at a given input concentration in order to facilitate later removal by various scrubbing processes.

APPENDIX B. DETERMINATION OF OZONE DEMAND

In order to obtain a quantitative estimate of the amount of ozone required to convert NO to NO_2 or N_2O_5 in a flue gas stream, a model will be developed for the process. Then the model will be used to estimate the amount of O_3 required for various flue gas rates and NO_x concentrations.

Model Reactor

The classical reactor situation of "plug flow" will be used for the model. As shown in Figure 9, an elemental volume, dV, in the reactor is considered. The total volume rate of flow, q, is considered constant into and out of the volume. Each species under consideration moves into dV at a rate qC_i, where C_i represents the volume concentration, in moles/m^3, of species i. In dV chemical reactions occur which change the concentration by ΔC_i so that the exit flow rate from dV is $q(C_i + \Delta C_i)$. For each dV the continuity relation for each species is[2]:

$$(\text{accumulation})_i = (\text{input})_i - (\text{output})_i + (\text{generation})_i - (\text{recombination})_i . \tag{B.1}$$

Since there is no provision for mass storage, the left hand side of (B.1) is identically zero. The modeling method consists of setting up the simultaneous equations of the form (B.1) with appropriate terms for each species and solving these, subject to the appropriate boundary conditions on input, in order to determine, for a given total reaction volume, V_o, the value of the concentrations of each species at the output.

In terms of rates, equation (B.1) can be written as

$$q \frac{\partial C_i}{\partial z} = \left[\left(\frac{\partial C_i}{\partial z}\right)_{gain} - \left(\frac{\partial C_i}{\partial t}\right)_{loss}\right] A \tag{B.2}$$

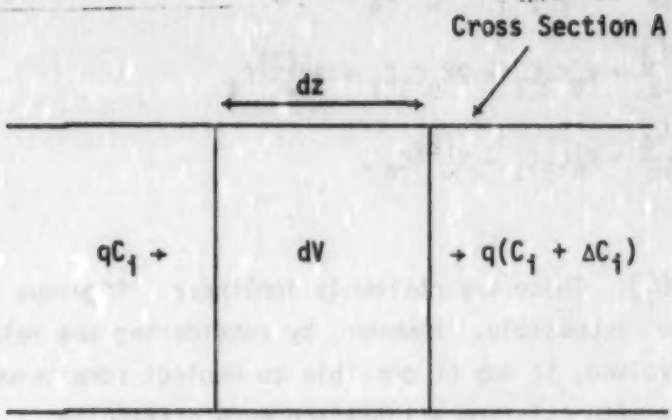

Figure 9. Elemental reaction volume in plug-flow reactor model.

where A is the cross-sectional area of the reactor. If the lineal velocity of transport is assumed to be a constant, u, over A, this can be written as

$$u \frac{\partial C_i}{\partial z} = \left[\left(\frac{\partial C_i}{\partial t}\right)_{gain} - \left(\frac{\partial C_i}{\partial t}\right)_{loss}\right] \qquad (B.3)$$

for the four species of interest, with the notation

C_1 = ozone concentration, $[O_3]$, moles/m^3

C_2 = nitric oxide concentration, [NO], moles/m^3

C_3 = nitrogen dioxide concentration $[NO_2]$, moles/m^3

C_4 = nitrogen pentoxide concentration $[N_2O_5]$, moles/m^3.

The simultaneous equations are:

$$u \frac{\partial C_1}{\partial z} = -K_5' C_1^2 - K_8 C_2 C_1 - K_9 C_3 C_1 - K^{(3)} C_4^{2/3} C_1^{2/3} \qquad (B.4)$$

$$u \frac{\partial C_2}{\partial z} = -K_8 C_2 C_1 - K_\infty^{(2)} C_4 \qquad (B.5)$$

$$u \frac{\partial C_3}{\partial z} = K_8 C_2 C_1 - 2K_9 C_3 C_1 + 3K_\infty^{(2)} C_4 \qquad (B.6)$$

$$u \frac{\partial C_4}{\partial z} = K_9 C_3 C_1 - K_\infty^{(2)} C_4 , \qquad (B.7)$$

where $K_5' = K_5/[O_2]$. These are obviously nonlinear. Rigorous solution is difficult, if not impossible. However, by considering the relative size of the terms involved, it may be possible to neglect some terms in order to get an approximate solution without too much difficulty.

Approximate Equations

Two situations will be considered. First, the flue gas is initially cooled to 60°C -- the situation used in Japanese pilot plant operations[1] -- and second, the flue gas is not cooled from its normal exit temperature of about 149°C. Values for the rate coefficients in equations (B.4) - (B.7) corresponding to these two temperatures are shown in Table 9. It is obvious that the "worst case" of the two situations as far as possible retention on the nonlinear terms in (B.4) - (B.7) are concerned is the higher temperature situation, which will be taken.

In order to test for the relative size of the rate terms, two cases will be considered. For both it will be assumed that the flue gas feed is at 472 m^3/s with 600 ppm NO and 30 ppm NO_2 at 149°C. These conditions are typical for a coal-fired 500 MW generation unit. The first case assumes that the added ozone is at 1% by weight in air and the feed rate gives an ozone/nitric oxide mole ratio of 1.0. The second case assumes that the added ozone is at 1.7% by weight in oxygen. The initial value of N_2O_5 is assumed to be zero for both cases. The resulting values for the rate terms in equations (B.4) - (B.7) are shown in Table 10.

It is obvious that the effect of gas phase thermal decomposition of ozone, the term $K_5' C_1^2$, is small initially even at 149°C and will become even smaller as the ozone concentration decreases due to reactions with the nitrogen oxides. Therefore, this term can be dropped from equation (B.4) with negligible error. It also appears that, as a first approximation, the interactions of N_2O_5 formation and reaction with NO and O_3

Table 9. Size of Reaction Rate Values at 60° and 149°C.

Reaction Rate	Pre-exponential Factor	Exponential Argument	Value at 60°C	Value at 149°C	Units
K_5'	$4.55 \times 10^{15}/[O_2]$	-15,400/T	$3.7 \times 10^{-5}/[O_2]$	$0.64/[O_2]$	Sec^{-1}
K_8	7.8×10^5 4.3×10^5	- 2,103/T - 1,173/T	1.41×10^4	3.2×10^4	m^3/mole-sec
K_9	5.9×10^9	- 3,523/T	1.5×10^2	1.4×10^3	m^3/mole-sec
$K^{(3)}$	2.23×10^{13}	-10,316/T	0.784	540	$(m^3/mole)^{+1/3}$ sec^{-1}
$K_\infty^{(2)}$	5.77×10^{14}	-10,568/T	9.5	7.68×10^3	Sec^{-1}

Table 10. Numerical Estimates for Initial Values at 149°C of Terms in Rate Equations at Stoichiometric Ozone Feed from Both Air Stock and Oxygen Stock

Terms	Feed Composition	
	1% (wt) Ozone in Air	1.7% (wt) Ozone in Oxygen
$K_5' C_1^2$	3.1×10^{-4}	1.2×10^{-4}
$K_8 C_2 C_1$	8.1	8.9
$K_9 C_3 C_1$	8.9×10^{-3}	9.7×10^{-3}
$K^{(3)} C_4^{2/3} C_1^{2/3}$	0	0
$K_\infty^{(2)} C_4$	0	0

can be neglected. This assumption will be tested after the simplified reaction equations are used to model the system.

The approximate rate equations can be written in the form

$$\frac{dC_1}{dz} = -aC_1C_2 - bC_1C_3 \tag{B.8}$$

$$\frac{dC_2}{dz} = -aC_1C_2 \tag{B.9}$$

$$\frac{dC_3}{dz} = aC_1C_2 - 2bC_1C_3 \tag{B.10}$$

$$\frac{dC_4}{dz} = bC_1C_3 \tag{B.11}$$

where $a = K_8/u$ and $b = K_9/u$.

Solution of Approximate Equations

These coupled nonlinear equations would still be extremely difficult to solve by conventional means. However, Benson[25] has discussed a method that provides a convenient way to assess the ratios of species concentrations when the reactions are allowed to proceed to a given extent. Using this method, it can be shown that the reactant concentrations can be written in the forms

$$\left(\frac{C_{10} - C_1}{C_{10}}\right) = \left\{\left(\frac{C_{20}}{C_{10}}\right)\left(\frac{3K-2}{2K-2}\right)\left(1 - \frac{C_2}{C_{20}}\right) + 0.5\left(\frac{C_{30}}{C_{20}} - \frac{1}{K-1}\right)\left[1 - \left(\frac{C_2}{C_{20}}\right)^K\right]\right\}, \tag{B.12}$$

$$\frac{C_{30}}{C_3} = \frac{C_{30}/C_{20}}{\left[\left(\frac{C_{30}}{C_{20}} - \frac{1}{K-1}\right)\left(\frac{C_2}{C_{20}}\right)^K + \frac{C_2/C_{20}}{K-1}\right]}, \tag{B.13}$$

and

$$\frac{C_4}{C_{30}} = \left(\frac{C_{20}}{C_{30}}\right)\left\{\frac{1}{2}\left(\frac{C_{30}}{C_{20}} - \frac{1}{K-1}\right)\left[1 - \left(\frac{C_2}{C_{20}}\right)^K\right] + \frac{K/2}{K-1}\left(1 - \frac{C_2}{C_{20}}\right)\right\}, \qquad (B.14)$$

where C_{10}, C_{20}, and C_{30} are the initial concentrations of ozone, nitric oxide, and nitrogen dioxide, respectively. It has been assumed that the initial concentration of N_2O_5 is zero. The parameter K is given by

$$K = 2\, K_9/K_8 . \qquad (B.15)$$

These equations can be used, with appropriate values for the initial concentrations of reactants, to determine the course of the reactions as NO and NO_2 are oxidized.

Numerical evaluations for the conditions:

$$T = 422°K\ (149°C)$$
$$C_{30}/C_{20} = 30/600 = 0.05$$
$$C_{10}/C_{20} = 0.5,\ 0.9,\ 1.0,\ \text{and}\ 1.1$$

are presented graphically in Figures 10, 11, 12, and 13. For the NO_x concentration ratio assumed, exact stoichiometry would require C_{10}/C_{20} to be 1.025. Comparison of the curves indicates that as far as NO oxidation in concerned, there is little advantage in exceeding the stoichiometric ratio. An increase of 10% added ozone, going from $C_{10}/C_{20} = 1.0$ to $C_{10}/C_{20} = 1.1$, results in only a slight increase in amount oxidized--i.e., from 96% to 98%. Most of the extra ozone is consumed in the production of N_2O_5.

Checking the assumption that led to dropping the C_4 terms from equations (B.4) - (B.7), consider the data of Figure 12 for the case where 90% of the ozone has been depleted. The rate terms of (B.4) - (B.11) are, for the case of air feed,

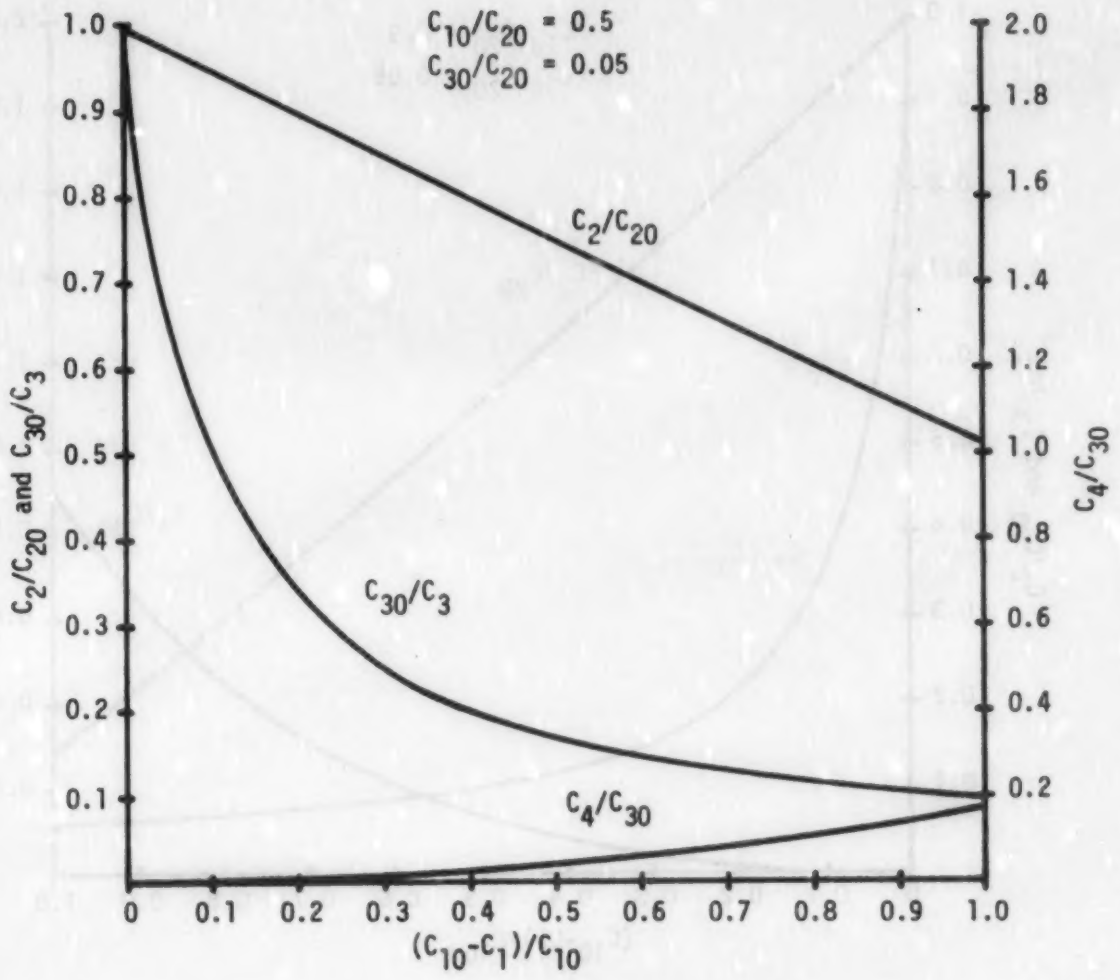

Figure 10. Relation between NO, NO_2 and N_2O_5 concentrations and the fraction of ozone used for oxidation for initial conditions $[O_3]/[NO]$ = 0.5 and $[NO_2]/[NO]$ = 0.05.

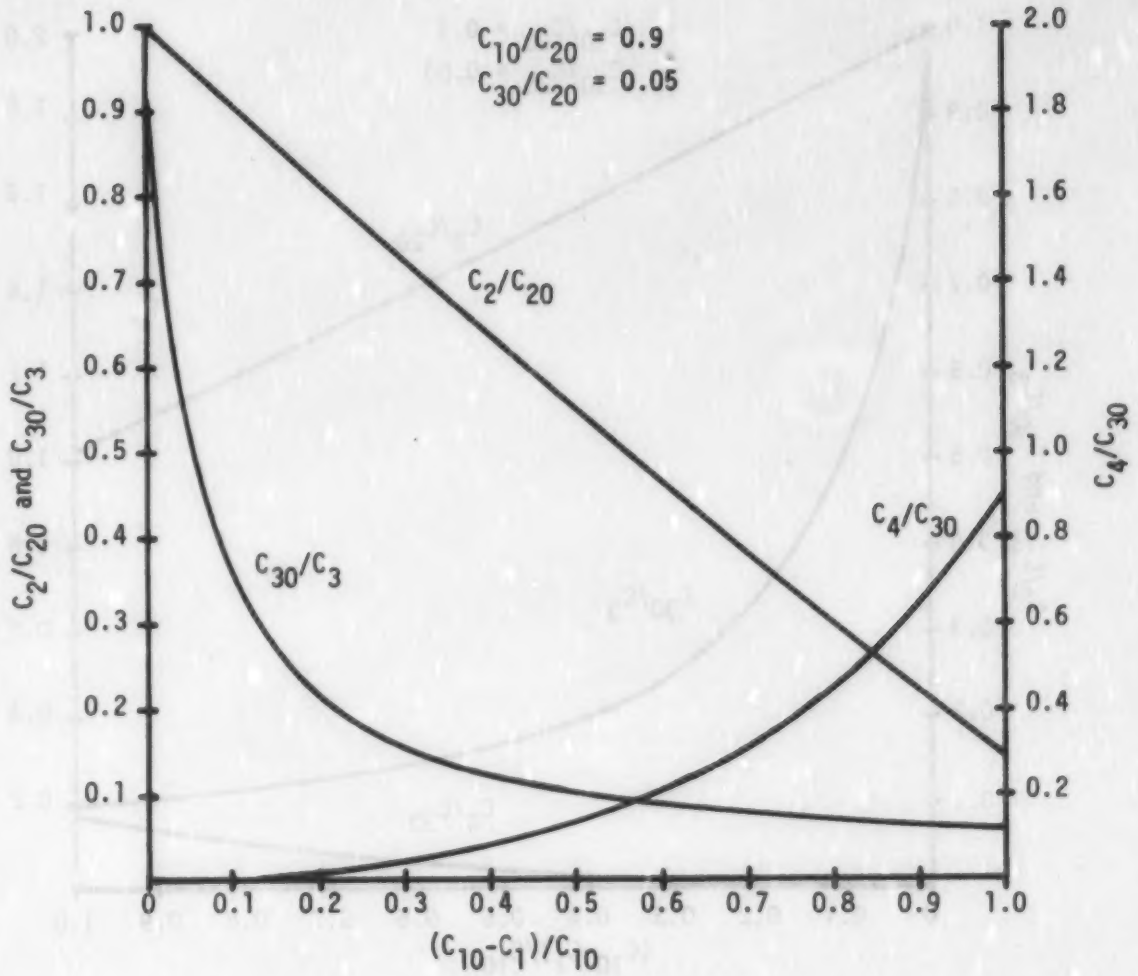

Figure 11. Relation between NO, NO_2 and N_2O_5 concentrations and the fraction of ozone used for oxidation for initial conditions $[O_3]/[NO]$ = 0.9 and $[NO_2]/[NO]$ = 0.05.

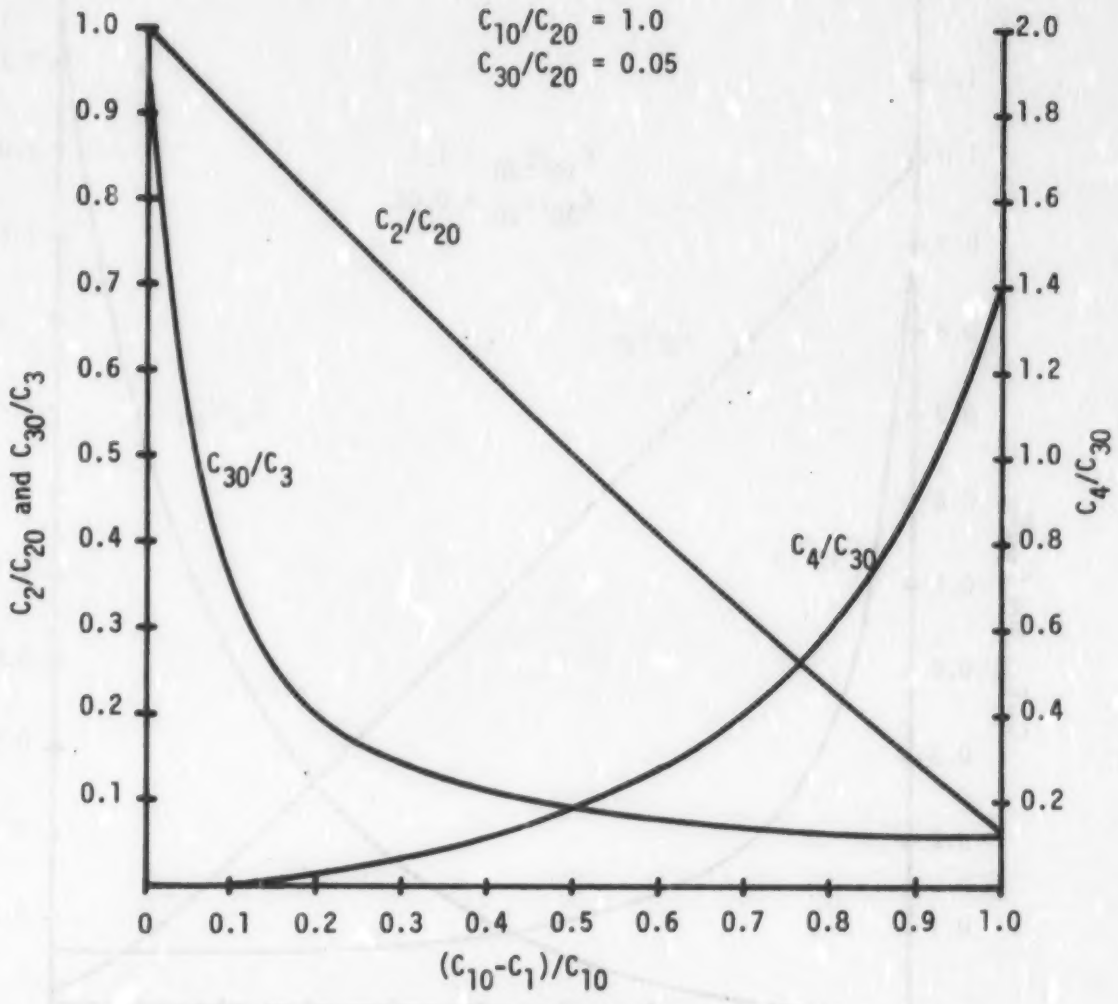

Figure 12. Relation between NO, NO_2 and N_2O_5 concentrations and the fraction of ozone used for oxidation for initial conditions $[O_3]/[NO]$ = 1.0 and $[NO_2]/[NO]$ = 0.05.

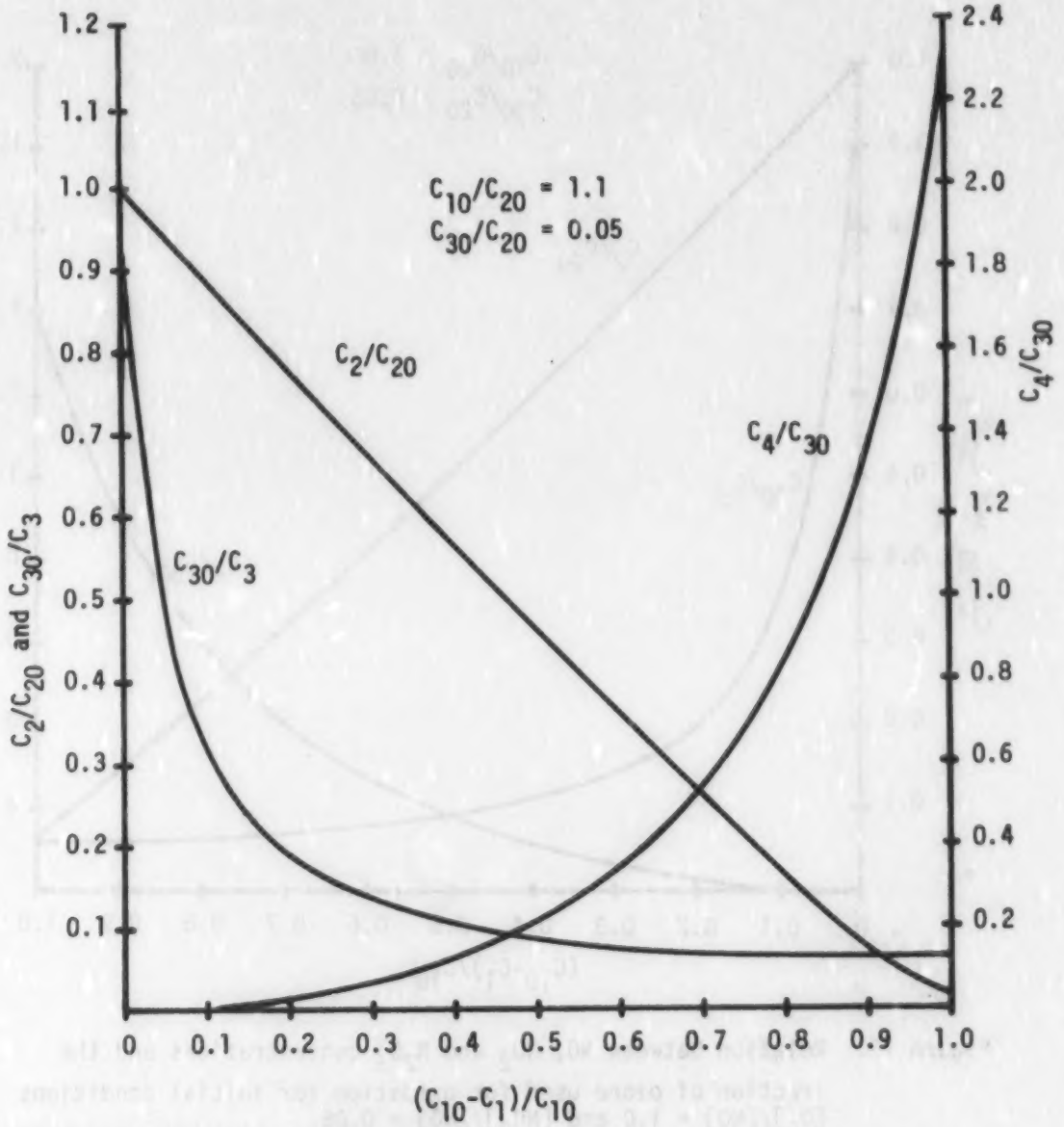

Figure 13. Relation between NO, NO_2 and N_2O_5 concentrations and the fraction of ozone used for oxidation for initial conditions $[O_3]/[NO]$ = 1.1 and $[NO_2]/[NO]$ = 0.05.

$$K_8C_1C_2 = 0.111 \qquad K_\infty^{(2)}C_4 = 2.73$$

$$K_1C_1C_3 = 0.0146 \qquad K^{(3)}(C_1C_4)^{2/3} = 0.0367 .$$

Thus, it appears that the assumption was not justified by these results because of the rapid build-up of N_2O_5 as the ozone nears depletion. The question arises as to whether or not such a build-up will occur since, according to equation (B.7),

$$u\frac{\partial C_4}{\partial z} = k_9C_1C_3 - K_\infty^{(2)}C_4 , \qquad (B.7)$$

the rate of increase of C_4 will be limited by its conversion to NO_2 through reaction with NO. As discussed in Appendix A, in connection with the inequality (A.22), as long as even small amounts of NO are present, they will rapidly react with N_2O_5 to produce NO_2. In the words of Benson, "NO acts as an efficient scavenger for N_2O_5."

Steady State Approximation

Taking this into account an alternative approach is to invoke the "steady-state hypothesis"[25] for the species N_2O_5. This hypothesis assumes that there is a rapid build-up of N_2O_5 to a concentration value where the two opposing rate terms in (B.7) balance to give a net rate of zero. When (and if) this occurs, the dynamic equilibrium value of C_4 is

$$C_4 = \frac{K_9}{K_\infty^{(2)}} C_1C_3 . \qquad (B.12)$$

Defining $f = K^{(3)}/u$ and $g = K_\infty^{(2)}/u$, the rate equations (B.4) - (B.7) can be written in the form

$$\frac{dC_1}{dz} = -aC_1C_2 - bC_1C_3 - f(C_1C_4)^{2/3} \qquad (B.13)$$

$$\frac{dC_2}{dz} = -aC_1C_2 - gC_4 \tag{B.14}$$

$$\frac{dC_3}{dz} = aC_1C_2 - 2\,bC_1C_3 + 3\,gC_4 \tag{B.15}$$

$$\frac{dC_4}{dz} = bC_1C_3 - gC_4 = 0\,. \tag{B.16}$$

Solving equation (B.16) for C_4 and substituting this into (B.13) - (B.15) gives

$$\frac{dC_1}{dz} = -aC_1C_2 - bC_1C_3 - f\left(\frac{b}{g}\,C_1^2C_3\right)^{2/3} \tag{B.17}$$

$$\frac{dC_2}{dz} = -aC_1C_2 - bC_1C_3 \tag{B.18}$$

$$\frac{dC_3}{dz} = aC_1C_2 + bC_1C_3\,. \tag{B.19}$$

Again using the situation of air feed to the ozone generator and a flue gas temperature of 149°C, the rate terms in the above equation can be compared for the situation where the C_1, C_2, and C_3 concentrations are near their initial value and C_4 has achieved its steady-state value of

$$C_4 = \frac{K_9}{K_\infty^{(2)}}\,C_1C_3 = 1.16 \times 10^{-6}\ \text{moles/m}^3\,.$$

The rate terms are

$$aC_1C_2 = \frac{K_8}{n}\,C_1C_2 = 8.11/u$$

$$bC_1C_3 = \frac{K_9}{u}\,C_1C_3 = 8.86 \times 10^{-3}/u$$

$$f(C_1C_4)^{2/3} = \frac{K^{(3)}}{u}(C_1C_4)^{2/3} = 3.82 \times 10^{-3}/u\,.$$

The last term is certainly negligible with respect to the first term, initially. As the concentration of NO_2, C_3, increases, the first term will decrease and the second term will increase, but not rapidly, since the build-up of C_3 is countered by the decrease of C_1. It will be assumed that the third term remains negligible and this assumption will be tested when the consequences are evaluated. With this modification, equations (B.17) - (B.19) are equivalent to

$$dC_2/dC_1 = 1 \tag{B.20}$$

$$dC_3/dC_1 = -1\,. \tag{B.21}$$

Using the initial conditions

$$\left.\begin{aligned} C_1 &= C_{10} \\ C_2 &= C_{20} \\ C_3 &= C_{30} \end{aligned}\right\} \quad \text{at } z = 0\ (t = 0)\,. \tag{B.22}$$

the NO and NO_2 concentrations are given by

$$C_2/C_{20} = 1 - (C_{10}/C_{20})(C_{10} - C_1)/C_{10} \tag{B.23}$$

$$C_3/C_{20} = (C_{30}/C_{20}) + (C_{10}/C_{20})(C_{10} - C_1)/C_{10}\,. \tag{B.24}$$

A plot of these relations for the case $C_{10}/C_{20} = 1.0$ and $C_{30}/C_{20} = 0.05$ is given in Figure 14.

Testing the assumption that the rate term $f(C_1C_4)^{2/3}$ remains negligible with respect to the other terms in equation (B.17), at 99% ozone use,

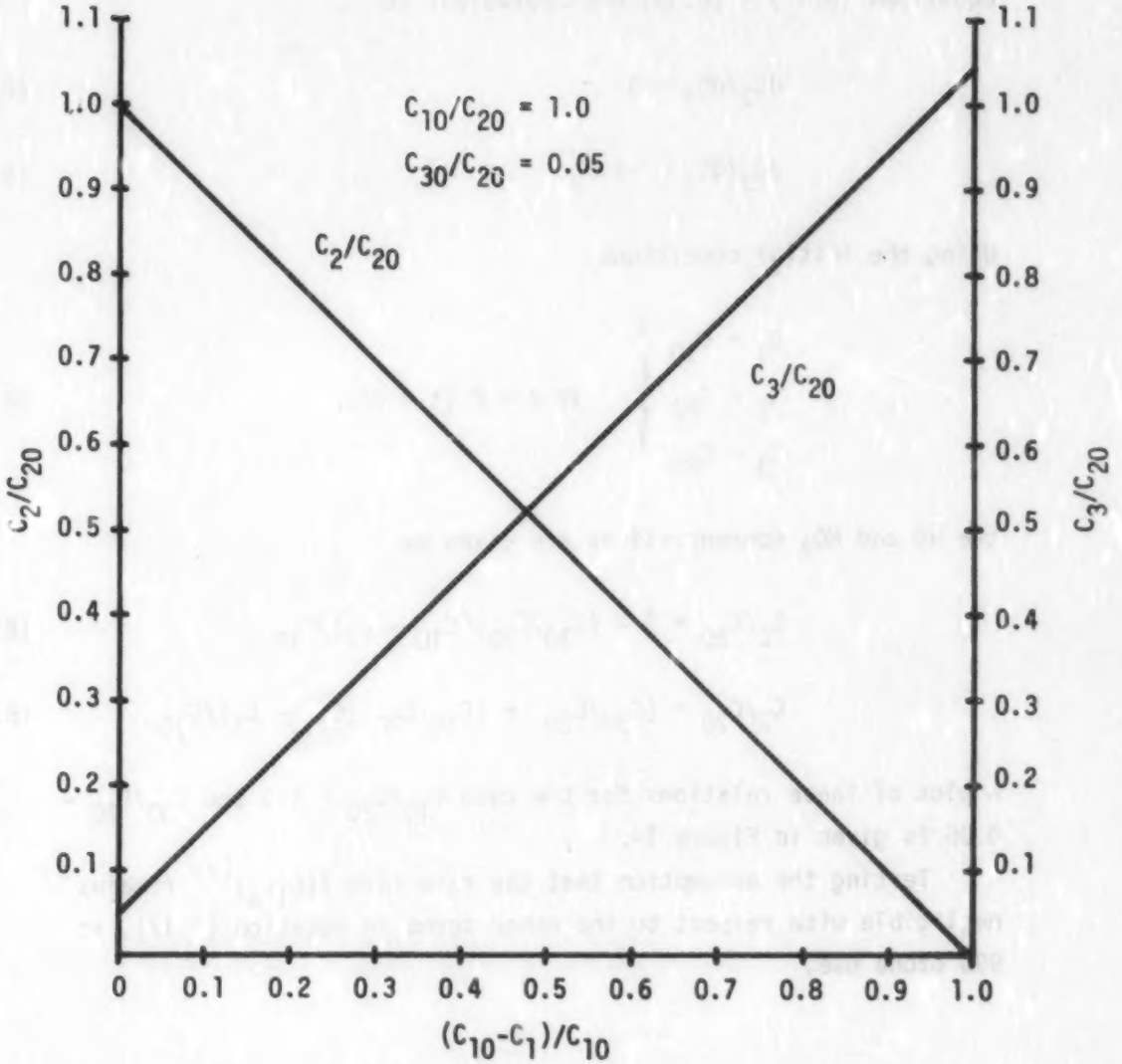

Figure 14. Relation between NO and NO_2 concentrations and the fraction of ozone used for initial conditions $[O_3]/[NO] = 1.0$ and $[NO_2]/[NO] = 0.05$ with steady state assumption for $[N_2O_5]$.

$$(C_{10} - C_1)/C_{10} = 0.99 \qquad C_2 = 0.01\ C_{20}$$

$$C_3 = 1.04\ C_{20}$$

$$aC_1C_2 = 8.11 \times 10^{-4}/u$$

$$bC_1C_3 = 1.84 \times 10^{-2}/u$$

$$f(C_1C_4)^{2/3} = 1.77 \times 10^{-4}/u\ .$$

The N_2O_5 catalyzed decomposition of ozone accounts for only about 1% of the ozone depletion rate at this point. Therefore, the assumption that this term remains negligible was justified.

The conclusion reached from this analysis is that the amount of ozone required for oxidation of NO to NO_2 is the amount required by the stoichiometric equation

$$O_3 + NO = NO_2 + O_2\ .$$

For a flue gas flow rate of Q_F m^3/sec and an NO concentration of n ppm, the mass flow rate of ozone required is

$$w_{O_3} = \frac{dm}{dt} = 2 \times 10^{-6}\ Q_F n\ . \quad \text{kg/sec} \qquad (B.25)$$

where Q_F is the flue gas rate under the industrial standard condition of 21°C (~70°F). For a 500-MW plant with a nominal flue gas flow rate of 1×10^6 SCFM or 472 m^3/sec with an NO concentration of 600 ppm, an ozone feed rate of 0.566 kg/sec or 53.9 tons/day is required. The ozone requirements for various flue gas flow rates at various NO concentrations have been plotted in Figure 1 of this report.

In closing, it should be re-emphasized that this model is for gas phase reactions only and does not account for wall losses of ozone. Inherent assumptions are those for the classical "plug flow" model--i.e., a uniform velocity across the reactor cross-section, good initial mixing of the reactants, and negligible axial diffusion effects.

APPENDIX C. ECONOMIC ANALYSIS

In order to determine the cost of oxidizing NO to NO_2 using ozone, the initial capital investment required for the construction of a suitably sized ozone generation plant must be estimated. Then the costs associated with amortization of the capital investment, labor, utilities, maintenance, etc., must be estimated and averaged over the amount of NO oxidized and over the amount of electric power generated over some suitable period of time. These measures can then be compared to other per unit generation cost measures in order to assess the economic viability of this method of NO oxidation vis-à-vis other methods.

Capital Costs

Capital investment cost can be estimated for both air feed and oxygen feed plants as follows. For tonnage-sized ozone plants the current costs of equipment plus direct construction costs run about $330 per kg ozone per day ($300,000/ton/day) using air feed.[8] This cost includes all of the air induction, drying, and cooling equipment necessary to condition the feed to the ozonators.

For oxygen feed there are two cost components, the ozone generation system and the oxygen plant. The ozone generation costs are estimated[8] to be $177 per kg O_3 per day ($160,000/ton/day). To this must be added the cost of building an oxygen plant to supply the feed. Oxygen plant cost can be estimated by obtaining a cost figure, C_1, for a plant of capacity Q_1 and extrapolating by the well-known cost-capacity relation

$$C_2 = C_1(Q_2/Q_1)^N \qquad (C.1)$$

where C_2 is the cost of a plant of capacity Q_2 and N is an exponent for a given class of equipment or process plant. The value of this exponent is determined by plotting cost-versus-size data on a log-log scale. Tables are published from time to time in various magazines and books germane to chemical engineering, which give values of N over a suitable size range for various equipments. In addition to the size factor of cost, there is

a price escalation factor which must be taken into account. The cost C_1 is for some base year with a cost index I_1. Plant of cost C_2 is to be built in a year with a cost index I_2, giving an updated cost of

$$C_2' = C_2 I_2 / I_1 = C_1 \frac{I_2}{I_1} (Q_2/Q_1)^N . \qquad (C.2)$$

For the current analysis a 1976 cost index is used for I_2. For oxygen plants in the range of about 900 kg/day to about 1.4×10^6 kg/day, Zimmerman[13] has given a value for N of 0.72, which is used in this analysis. Cost index data are obtained from Chemical Engineering magazine.[12]

For a 500-MW coal-fired plant with a nominal NO concentration of 600 ppm, the required ozone is, from the analysis of Appendix B, 49,000 kg/day (53.9 tons/day). For a 500-MW oil-fired plant with a nominal concentration of 200 ppm, the requirement is about 16,300 kg/day (18 tons/day). Assuming 1.7% by weight ozone when oxygen is used as a feedstock to the ozonators, the required oxygen plant capacities are 2.9×10^6 kg/day (3180 tons/day) and 9.67×10^5 kg/day (1060 tons/day), respectively. The latter figure lies within the range given by Zimmerman corresponding to N = 0.72 for the cost capacity equation (C.1). The larger plant, however, is over twice the size of the upper range limit. For the cost estimate for this size plant, it will be assumed that two parallel plants at the upper limit (or only slightly above) are to be built as a unit to obtain a direct cost figure. Using data for a mid-1974 oxygen plant of 7.89×10^5 kg/day (870 tons/day) capacity, the oxygen plant costs are

$$\text{Oil-fired case: } C_2 = \$11 \times 10^6 \left(\frac{1060}{870}\right)^{0.72} = \$12.7 \text{ million}$$

$$\text{Coal-fired case: } C_2 = 2 \times \$11 \times 10^6 \left(\frac{1590}{870}\right)^{0.72} = \$34 \text{ million}$$

These direct costs, updated to first quarter 1976 dollars using Chemical Engineering magazine indices, are given in Table 11 along with the ozone generator direct costs.

Table 11. Estimated Direct Capital Costs for Ozone Generation for NO Oxidation in 500-MW Generating Stations

Type/NO Concentration	Ozone Required (kg/day)	Direct Capital Costs			
		Air Feed	Oxygen Feed		
			Ozonator	O_2 Plant	Total
Oil Fired/ 200 ppm	16,300	$ 5.4 M	$2.9 M	$14.4 M	$17.3 M
Coal Fired/ 600 ppm	49,000	$16.2 M	$8.6 M	$38.4 M	$47 M

In addition to these direct costs, which include equipment, installation, labor and materials, and construction facilities, there are indirect project costs that must be added into the total investment. These costs include engineering and design supervision, construction field expense, contractor's fees, contingency, allowance for start-up and modification, and interest during construction. The figures used for these items, shown in Table 12 taken from McGlamery et al.,[3] are representative of those expected for power industry equipment installation. In addition to the percentage contributions shown in Table 11, it is standard practice to include an allowance for start-up and modification costs, which will be taken as 8% of the subtotal direct plus indirect investment, and to include the interest costs during construction. The interest cost is estimated to be 10% per year, and the construction is assumed to take place over a three-year period, giving a cumulative rate of 12% direct plus indirect investment.

McGlamery et al.[3] assumed a capital structure of 50% equity - 50% debt for their calculations with a three-year project expenditure schedule. This does not agree with recent practice. In 1974 only 33% of construction funds were provided internally with the percentage expected to rise to about 41% by 1979.[26] Using 40% equity - 60% debt financing at 10% simple interest, the project expenditure schedule is as shown in Table 13. The cumulative debt financing is equivalent to 12% of the total expenditure, which was the value used to compute the interest during construction costs in Table 7.

Table 12. Indirect Investment and Allowance Factors

Power unit size and status	Percentage of direct investment 500 MW	
	New	Existing
Engineering design and supervision	9	10
Construction field expense	11	13
Contractor's fees	5	7
Contingency[a]	10	11
Total indirects	35	41

[a]Based on proven design rather than a "first of a kind" installation; a minimum amount of contingency is included. For a "first of a kind" installation, contingency would normally be greater than that shown above.

Table 13. Project Expenditure Schedule

Item	Year			
	1	2	3	Total
% of expenditure as borrowed funds	15	30	15	60
Simple interest at 10%/year as % of total expenditure				
Year 1 debt	1.5	1.5	1.5	4.5
Year 2 debt	--	3.0	3.0	6.0
Year 3 debt	--	--	1.5	1.5
Accumulated interest as % of total expenditure	1.5	4.5	6.0	12.0

It has been assumed that the plant equipment shown in Table 11 will be installed only in new plants. Based on this assumption and the use of the corresponding percentages for indirect costs shown in Table 12, the estimated total capital investment is as shown in Table 7 of the text. These estimates are in 1976 dollars.

Operating Costs

For an estimation of operating costs, the procedure that will be used will generally follow the method of McGlamery et al.[13] The cost elements will be divided into three categories: direct costs, indirect costs, and fixed costs (average capital charges). Direct cost elements for the process options are given in Table 13. The cost of power is taken as 2 cents/kWh for coal-fired units and 3 cents/kWh for oil-fired units.[27] The cost of cooling water depends on the usage rate. A plot of cost versus rate[27] is shown in Figure 15. Costs were taken to nearest cent from this data. The indirect costs are figured on the basis of a plant overhead, 20% of the total direct costs, and an administrative overhead, 10% of the direct labor cost. The average capital charges which constitute the fixed costs are compiled in Table 15. These differ somewhat from the figures used by McGlamery et al. because the capital structure is assumed to be 60% debt - 40% equity rather than 50/50. In addition, it is assumed that 0.5% of the original investment will be allowed for interim replacements rather than 0.6%.

Based upon these cost elements, calculations were made of operating costs for the first year on the basis of 7000 hours of operation (cf. Table 6). During this first year, the fixed costs are at a maximum because the base is the initial investment. The figures for each cost element, as well as unit costs, in terms of dollars per kg of O_3 produced and in terms of mils per generated kilowatt-hour, are given in Table 8 of the text.

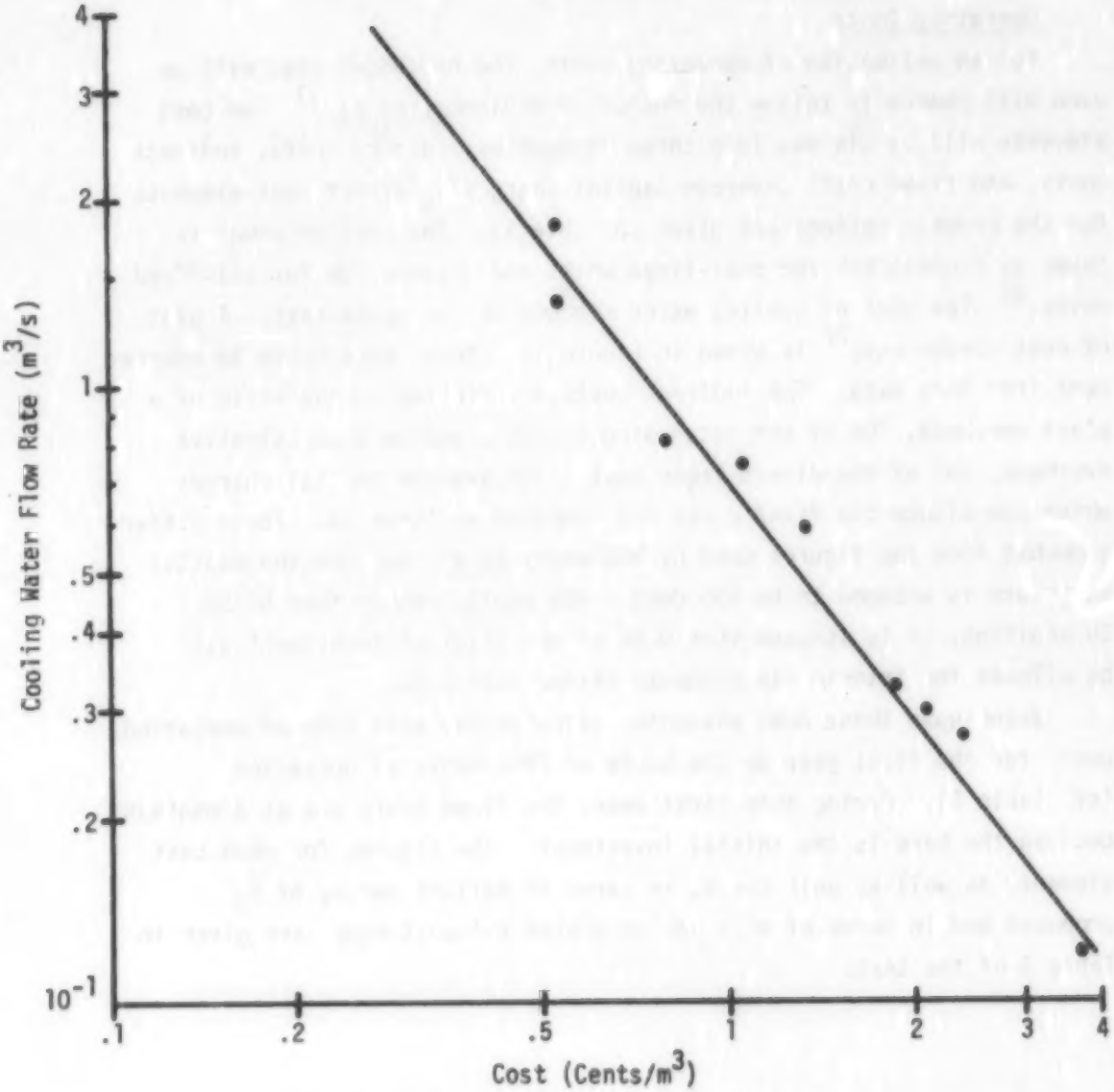

Figure 15. Cost of cooling water versus flow rate.

Table 14. Direct Cost Elements for Operation of Ozonators and Oxygen Plant

Ozonators (Air Feed):

Electric Power: $23{,}148 \left(\frac{\text{kWh}}{1000 \text{ kg } O_3}\right) \times \text{Capacity} \left(\frac{1000 \text{ kg } O_3}{\text{day}}\right) \times \frac{\text{Cost}}{\text{kWh}} \times \frac{\text{days of operation}}{\text{yr}}$

Cooling Water: $1{,}400 \left(\frac{m^3}{1000 \text{ kg } O_3}\right) \times \text{Capacity} \left(\frac{1000 \text{ kg } O_3}{\text{day}}\right) \times \frac{\text{Cost}}{m^3} \times \frac{\text{days of operation}}{\text{yr}}$

Labor: $48 \frac{\text{man-hr}}{\text{day}} \times \frac{365 \text{ days}}{\text{yr}} \times \frac{\$8.50}{\text{man-hr}}$ (oil-fired)

$96 \frac{\text{man-hr}}{\text{day}} \times \frac{365 \text{ days}}{\text{yr}} \times \frac{\$8.50}{\text{man-hr}}$ (coal-fired)

Maintenance: 6%/yr of direct investment cost

Ozonators (Oxygen Feed) and Oxygen Plant:

Electric Power: $\left[8267\left(\frac{\text{kWh}}{1000 \text{ kg } O_3}\right) \times \text{Capacity} \left(\frac{1000 \text{ kg } O_3}{\text{day}}\right) + 310 \left(\frac{\text{kWh}}{1000 \text{ kg } O_2}\right) \times \text{Capacity} \left(\frac{1000 \text{ kg } O_2}{\text{day}}\right)\right] \times \frac{\text{Cost}}{\text{kWh}} \times \frac{\text{days of operation}}{\text{yr}}$

Cooling Water: $\left[1{,}400 \left(\frac{m^3}{1000 \text{ kg } O_3}\right) \times \text{Capacity} \left(\frac{1000 \text{ kg } O_3}{\text{day}}\right) + 124.6 \left(\frac{m^3}{1000 \text{ kg } O_2}\right) \times \text{Capacity} \left(\frac{1000 \text{ kg } O_2}{\text{day}}\right)\right] \times \frac{\text{Cost}}{m^3} \times \frac{\text{days of operation}}{\text{yr}}$

Labor: $96 \frac{\text{man-hr}}{\text{day}} \times \frac{365 \text{ days}}{\text{yr}} \times \frac{\$8.50}{\text{man-hr}}$ (oil-fired)

$144 \frac{\text{man-hr}}{\text{day}} \times \frac{365 \text{ days}}{\text{yr}} \times \frac{\$8.50}{\text{man-hr}}$ (coal-fired)

Maintenance: 3%/yr of direct investment cost

Table 15. Annual Capital Charges for Power Industry Financing

Item	As % Original Investment
Depreciation-straight line basis	3.33
Interim replacements	0.5
Insurance	0.5
Total applied to original investment	4.33

Item	As % Outstanding Depreciation Base*
Cost of capital	
60% debt - bonds at 10%	6.0
40% equity - 14% return	5.6
Taxes	
Federal (50% of gross return)	5.6
State (National average)	4.5
Total applied to depreciation base	21.7

*Applied on an average basis over 30 years, the total annual % of fixed investment would be 4.33% + 1/2 (21.7%) = 15.18%.

REFERENCES

1. J. Ando, H. Tohata, and G. A. Issacs, "NO_x Abatement for Stationary Sources in Japan," Final Report on EPA Contract No. 68-02-1321, Task 6. EPA-600/2-76-013b. PEDCo Environmental Specialists, Inc., Cincinnati, Ohio, January 1976.

2. D. M. Himmelbau and K. B. Bischoff, Process Analysis and Simulation Deterministic Systems, John Wiley and Sons, New York, pp. 25-28.

3. G. G. McGlamery, et al., "Detailed Cost Estimates for Advanced Effluent Desulfurization Processes," EPA-600/2-75-006, U.S. Environmental Protection Agency Office of Research and Development, Washington, D.C., January 1975

4. J. A. Kerr and A. F. Trotman-Dickinson, "Strengths of Chemical Bonds," page F-149 in R. C. Weast (Ed.), Handbook of Chemistry and Physics, 48th Edition, The Chemical Rubber Co., Cleveland, Ohio, 1967.

5. T. C. Manley and S. J. Niegowski, "Ozone," pp. 410-432 in K. Othmer (Ed.), Encyclopedia of Chemical Technology, 2nd Edition, Volume 14, Interscience Publishers, New York, 1967.

6. M. J. Klein, et al., "Generation of Ozone," pp. 1-9 in R. G. Rice and M. E. Browning (Eds.), First International Symposium on Ozone for Water and Wastewater Treatment, International Ozone Institute, Waterbury, Conn. 1975.

7. "Ozone Generation for Industrial Application," Bulletin 201, The Welsbach Corporation, Ozone Processes Division, Philadelphia, Pa., May 1965.

8. Estimate by Mr. Carl Nebel, Welsbach Corporation, Ozone Processes Division, Philadelphia, Pa., June 2, 1976 and August 30, 1976.

9. J. F. Potter, Linde Division, Union Carbide, private communication, September 8, 1976.

10. H. M. Rosen, "Integrating Ozone Systems," pp. 843-851 in Rice and Browning, op cit.

11. Federal Power Commission, "Hydroelectric Power Evaluation," FPC P-35 (1968) and Supplement No. 1, FPC P-38 (1969), Superintendent of Documents, U.S. Government Printing Office, Washington, D.C.

12. Chemical Engineering, p. 7, May 24, 1976.

13. O. T. Zimmerman, "Capital Investment Cost Estimation," pp. 301-337 in F. C. Jelen (Ed.), Cost and Optimization Engineering, McGraw-Hill, New York, N.Y., 1970.

14. Private communication, Dr. Harvey Rosen, Union Carbide, February, 1976.

15. N. Okada, et al., "Preparation of Ozone," Japan Kokai, 73, 39, p. 391, June 9, 1973. (Chemical Abstracts, 79, P94131, 1973.)

16. M. Steinberg, et al., "Large Scale Ozone Production in Chemo-Nuclear Reactors for Waste Treatment," pp. 10-39 in Rice and Browning, op cit.

17. S. W. Benson and A. E. Axworthy, "Mechanism of the Gas Phase, Thermal Decomposition of Ozone," J. Chem. Phys., 26, 1718 (1957).

18. M. Gauthier and D. R. Snelling, "Possible Production of O_2 ($^1\Delta g$) and O_2 ($^1\Sigma_g^+$) in the Reaction of NO with O_3," Chem. Phys. Letters, 20, 178 (1973).

19. J. A. Ghormley, et al., "Reaction of Excited Oxygen Atoms with Nitrous Oxide. Rate Constants for Reaction of Ozone with Nitric Oxide and Nitrogen Dioxide," J. Phys. Chem., 77, 1341 (1973).

20. H. S. Johnson, "Four Mechanisms Involving Nitrogen Peroxide," J. Amer. Chem. Soc., 73, 4542 (1951).

21. G. Schott and N. Davidson, "Shock Waves in Chemical Kinetics: Nitrogen Peroxide," J. Amer. Chem. Soc., 80, 1841 (1958).

22. H. S. Johnson, Gas Phase Reaction Theory, The Ronald Press Co., New York, N.Y., 1966. pp. 14-32.

23. D. D. Davis, et al., "Stop Flow Time of Flight Mass Spectrometry Kinetics Study. Reactions of Ozone with Nitrogen Dioxide and Sulfur Dioxide," J. Phys. Chem., 78, 1775 (1974).

24. R. A. Cox and S. A. Paukett, "Aerosol Formation from Sulfur Dioxide in the Presence of Ozone and Olefinic Hydrocarbons," J. Chem. Soc., Faraday Transactions I, 68, 1735 (1972).

25. S. W. Benson, The Foundation of Chemical Kinetics, McGraw-Hill Book Co., New York, N.Y., 1960. Also see S. W. Benson, "The Induction Period in Chain Reactions," J. Chem. Phys., 20, 1605 (1952).

26. Federal Power Commission, "National Power Survey - The Financial Outlook for the Electric Power Industry," FPC P87 Report and Recommendations of the Technical Advisory Committee on Finance, Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., December 1974.

27. Private communication, D. Mobley, EPA-NERC, Research Triangle Park, N. C., August, 1976.